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Technology Transfer Program

**1st. Workshop
on**

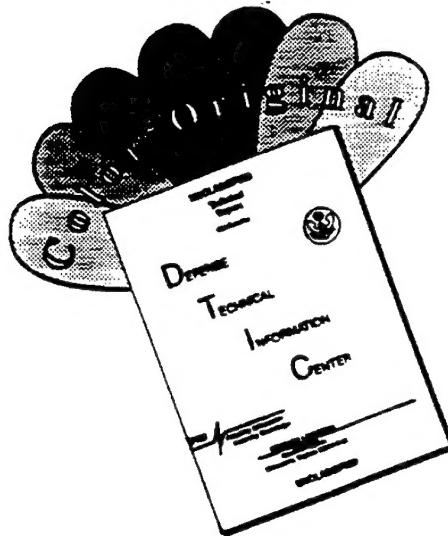
Frontiers of Advanced Materials and Technology

**Main Conference Hall- The National Research Centre
Dokki, Cairo, Egypt**

23 - 26, September, 1996

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Technology Transfer Program
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We wish to thank the United State Air Force European Office of Aerospace Research and Development for it's contribution to the success of this workshop.

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Speakers

Topics

Prof. Dr. Larry Hench

Chair of Ceramic Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK.

Dr. June Willson Hench, Distinguished Visitor, Department of Histopathology, Royal Free Hospital, University of London, London, England.

Bioactive Medical and Dental Materials

- 1) Clinical needs and types of biomedical materials.
- 2) Tissues and their reaction to implants.
- 3) Principles of bioactive bonding.
- 4) Medical and dental application of bioactive implants.

Prof. Dr. Larry Hench

Chair of Ceramic Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK.

Sol Gel Optics Technology:

- 1) Principles of sol-gel processing.
- 2) Gel silica optics, micro-optics and surface diffractive optics.
- 3) Porous gel silica matrices for hybrid optics.
- 4) Concepts of commercial principles of technology transfer and entrepreneurship.

Prof. Dr. Jacques Lucas

Universite' De Rennes 1, Laboratoire Des Verres et Ceramiques, Campus de Beaulieu, 35042 Rennes Cedex, France.

Infra-red Transmitting glasses:

- 1) glass forming systems.
- 2) Optical properties of IR glasses.
- 3) IR glass optical fibers.
- 4) Rare-earth doped glasses(optical amplifier, fiber laser).
- 5) IR glasses for integrated optics.

Prof. Dr. Hendrikus De Waal

Grabijnhof 35, 2625 LM Delft
The Netherlands.

Fundamentals of Industrial glass

melting:

- 1) Introduction into Modern Glass Manufacturing.
- 2) Batch Melting.
- 3) The fining process.
- 4) Volatilization and dust formation in glass furnaces.
- 5) Foam formation during glass melting.

Prof. Dr. Carlo Pantano

Pennsylvania State University, Dept. of Material Science and Engineering,
123 Steidle, University Park, Penn. 16802,
USA.

Glass Surfaces:

- 1) Introduction.
- 2) Characterization of glass surfaces.
- 3) Surface Chemistry.
- 4) Manufacturing effects on glass surfaces.

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Monday ,September 23

09:00 - 10:00 Registration
10:00 - 10:30 Opening Session
10:30 - 11:30 Break
11:30 - 12:30 Sol Gel Optics Technology (1) L. Hench
12:30 - 13:30 Infra-red Transmitting glasses (1) J. Lucas
13:30 - 14:30 Bioactive Medical and Dental Materials (1) L. Hench
14:30 - 15:00 Lunch
15:00 - 16:30 Bioactive Medical and Dental Materials (2) J. W. Hench
16:30 - 17:30 Sol Gel Optics Technology (2) L. Hench

Tuesday , September 24

09:30 - 10:30 Infra-red Transmitting glasses (2) J. Lucas
10:30 - 11:30 Bioactive Medical and Dental Materials (3) L. Hench
11:30 - 12:30 Bioactive Medical and Dental Materials (4) J. W. Hench
12:30 - 13:00 break
13:00 - 14:00 Sol Gel Optics Technology (3) L. Hench
14:00 - 15:00 Infra-red Transmitting glasses (3) J. Lucas
15:00 - 15:30 Lunch
15:30 - 16:30 Sol Gel Optics Technology (4) L. Hench
16:30 - 17:30 Infra-red Transmitting glasses (4) J. Lucas

Wednesday , September 25

09:30 - 10:30 Fundamentals of Industrial glass melting (1) H. De Waal
10:30 - 11:30 Glass Surfaces (1) C. Pantano
11:30 - 12:30 Infra-red Transmitting glasses (5) J. Lucas
12:30 - 13:00 Lunch
13:00 - 14:00 Fundamentals of Industrial glass melting (2) H. De Waal
14:00 - 15:00 Glass Surfaces (2) C. Pantano
15:00 - 16:00 Fundamentals of Industrial glass melting (3) H. De Waal
18:30 -20:30 Official Banquet

Thursday , September 26

9:30 - 10:30 Glass Surfaces (3) C. Pantano
10:30 - 11:30 Fundamentals of Industrial glass melting (4) H. De Waal
11:30 - 12:00 break
12:00 - 13:00 Glass Surfaces (4) C. Pantano
13:00 - 14:00 Fundamentals of Industrial glass melting (5) H. De Waal
14:00 - 15:00 Closing Session

Lectures

(In brief)

SOL GEL OPTICS TECHNOLOGY

Lecture 1: PRINCIPLES OF SOL GEL PROCESSING

There are 7 processing steps involved in making products by low temperature sol gel chemical methods: 1) mixing, 2) casting, 3) gelation, 4) aging, 5) drying, 6) stabilization, and 7) densification. The physical chemical principles of each of these process steps are reviewed. Figure 1 summarizes the seven process steps and shows a schematic of the ultrastructural evolution that occurs during sol gel processing. The range of processing temperatures are also shown in Figure 1. Steps 1,2,3,4 occur at ambient temperature and therefore permit use of inexpensive molds and requires only small capital investment. Drying takes place in inexpensive controlled atmosphere ovens from 100 to 180 C. Chemical and thermal stabilization of sol gel products occurs at temperatures in the range of 800-1000C using standard ceramic furnaces. Following stabilization two types of new optical products can be made: 1) porosity can be eliminated to form a full density glass, called Type V Gel Silica (GELSIL®); or 2) the porosity can remain open and interconnected for use as a porous optical matrix, Type VI Gel Silica.

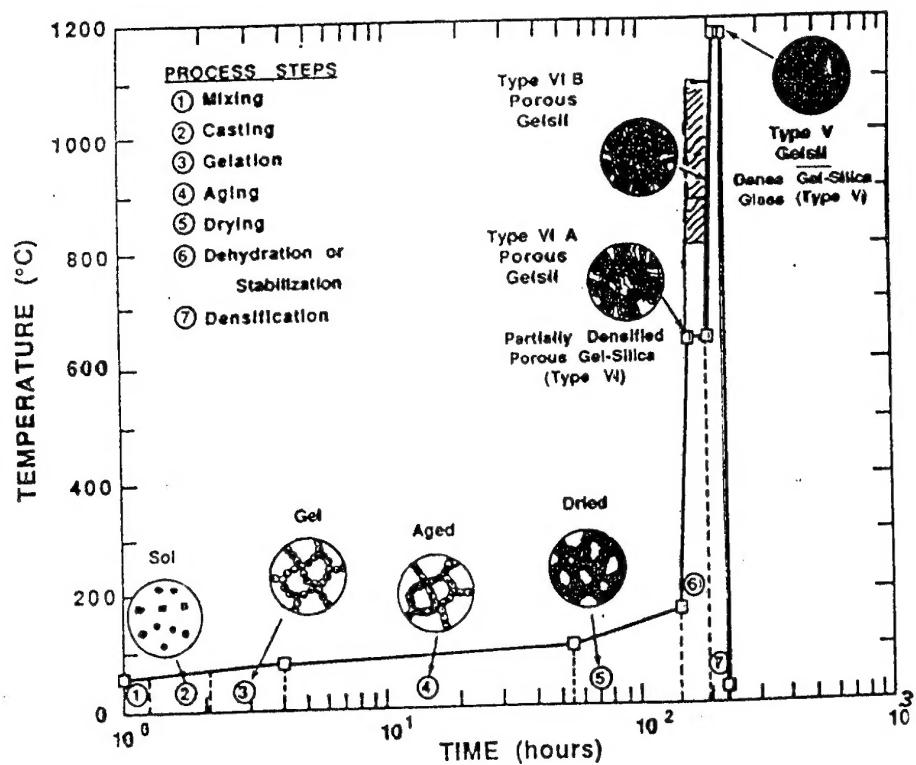


Fig. 1

Lecture 2: GEL-SILICA OPTICS. MICRO-OPTICS AND SURFACE DIFFRACTIVE OPTICS

Casting of silicon alkoxide derived sols into molds yields pure silica optical components with net shapes and net surfaces. The optical properties of gel-derived silica are superior to commercial optical silicas of Types I,II,III, and equivalent to the most expensive Type IV silicas. An important advantage of the sol gel method of making optical silica is elimination of costly and inaccurate slicing, grinding and polishing operations. A further advantage of gel-silica processing is the ability to replicate with very high precision surface features needed to produce micro-optics and surface diffractive optics. Replication of Fresnel lenslets of ± 0.1 micrometers can be achieved in full density silica, for example. Figure 2 shows examples of some of the net shape optical silica components made by the gel-silica process.

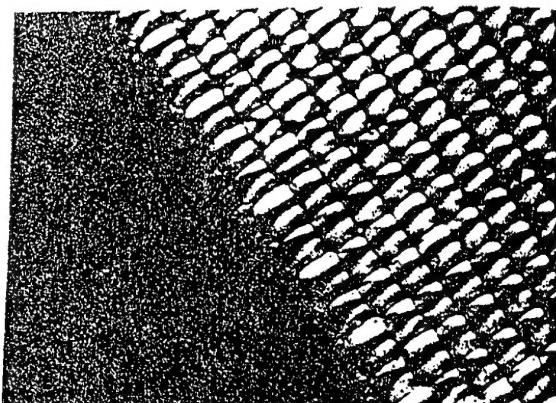


Figure A. High-fill-factor micro-lens array (lenslet space approx. 40 microns).

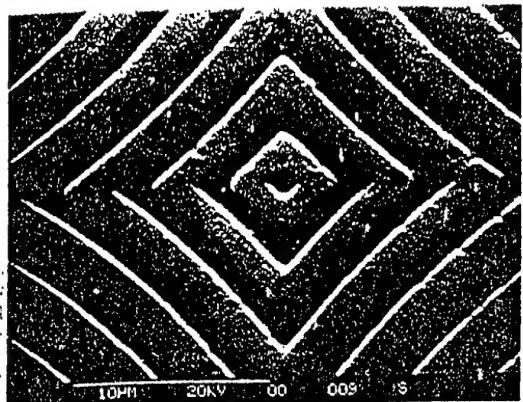


Figure B. Silica replicated binary optic (higher magnification).

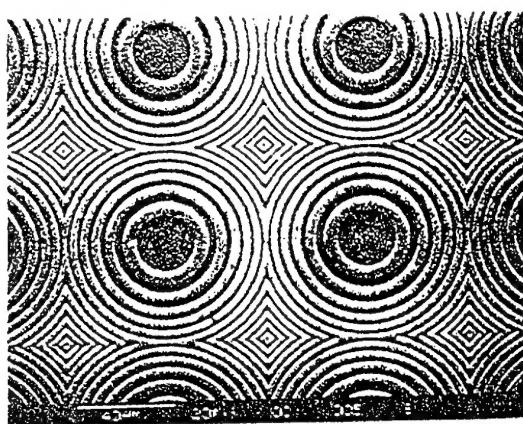


Figure C. Silica replicated binary optic (micro-lens array).

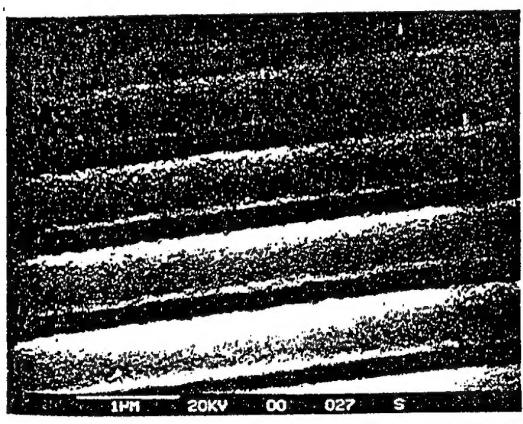


Figure D. Sol-gel silica replicated diffractive grating (line spacing is 0.9 μ m).

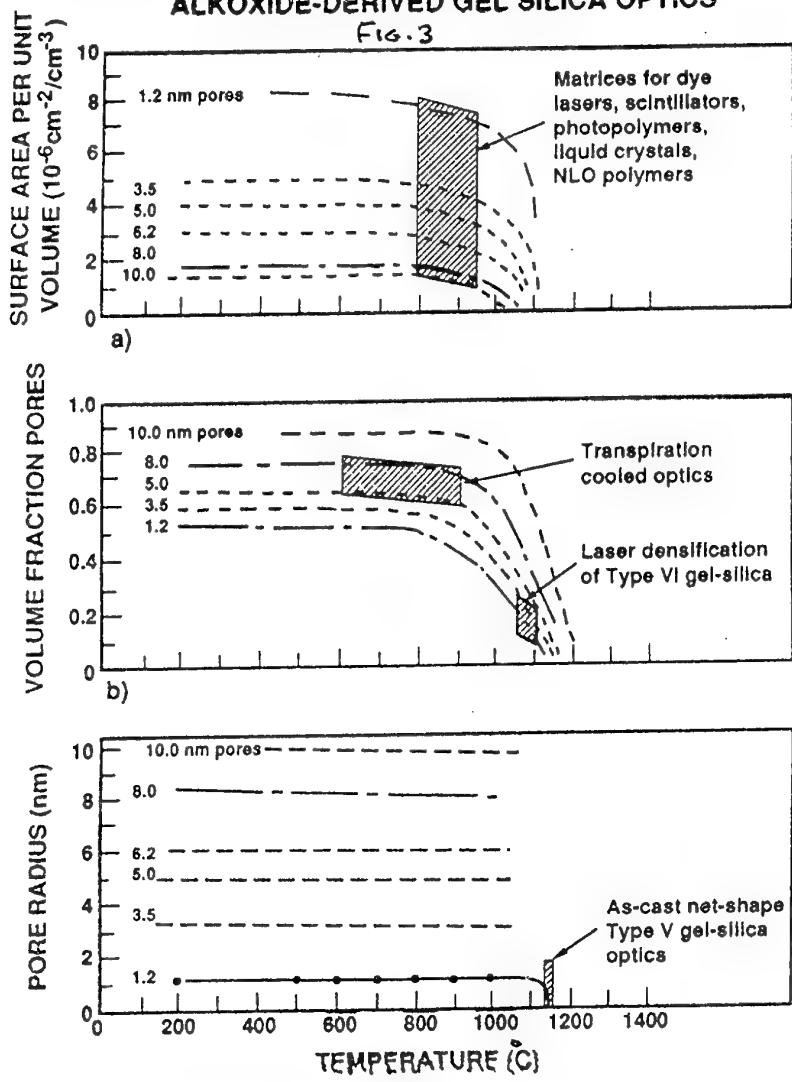
Fig. 2

Lecture 3: POROUS GEL SILICA MATRICES FOR HYBRID OPTICS

Control of the rates of hydrolysis and condensation reactions prior to gelation and control of the length of aging time, temperature and pH can be used to alter the size and size distribution of interconnected porosity in gel derived silica. Narrow pore size distributions of +/- 0.2 nm in the range of 1.2 to 12 nanometers result in optical materials that are transparent in the visible and near ultraviolet. The volume percentage of porosity can be controlled from as much as 80% to as low as 15%. See Figure 3 for the range of thermal history and textural properties of the porous gel silica matrices. The wide range of textures permits impregnation of the porous optical matrices with many different types of optically active second phases, creating a new generation of hybrid optics. Thermal and chemical stabilization temperatures also can be varied from 800 to 1000 C which controls the concentration of silanols and metastable trisiloxane rings on the porous gel silica surface. Interaction of these surface features with second phases is important in optimizing performance of a hybrid optical component. Examples, such as solid state dye lasers, toxic gas sensors, scintillation detectors and wavelength shifters, are discussed.

**VARIATION OF TEXTURE WITH TEMPERATURE FOR
ALKOXIDE-DERIVED GEL SILICA OPTICS**

Fig. 3



Lecture 4: FROM CONCEPT TO COMMERCE -PRINCIPLES OF TECHNOLOGY TRANSFER AND ENTREPRENEURSHIP

Developing a commercial business from new technology is difficult and expensive. Few university or government laboratories have the experience to circumvent the barriers encountered in technology transfer. Four primary pathways associated with a successful technology transfer process are described, as summarized in Figure 4. The pathways are: 1) Research, 2) Patent Protection, 3) Market Assessment, and 4) Technology Demonstration. The output of each of the paths is shown in Fig. 4 along with estimates of the costs involved and the time required to achieve an output. The concept of staggered parallel paths of technology transfer is described and the steps necessary to form a competitive start-up business. Examples from the field of sol-gel processing of optics and bioactive medical materials are used to illustrate the principles involved.

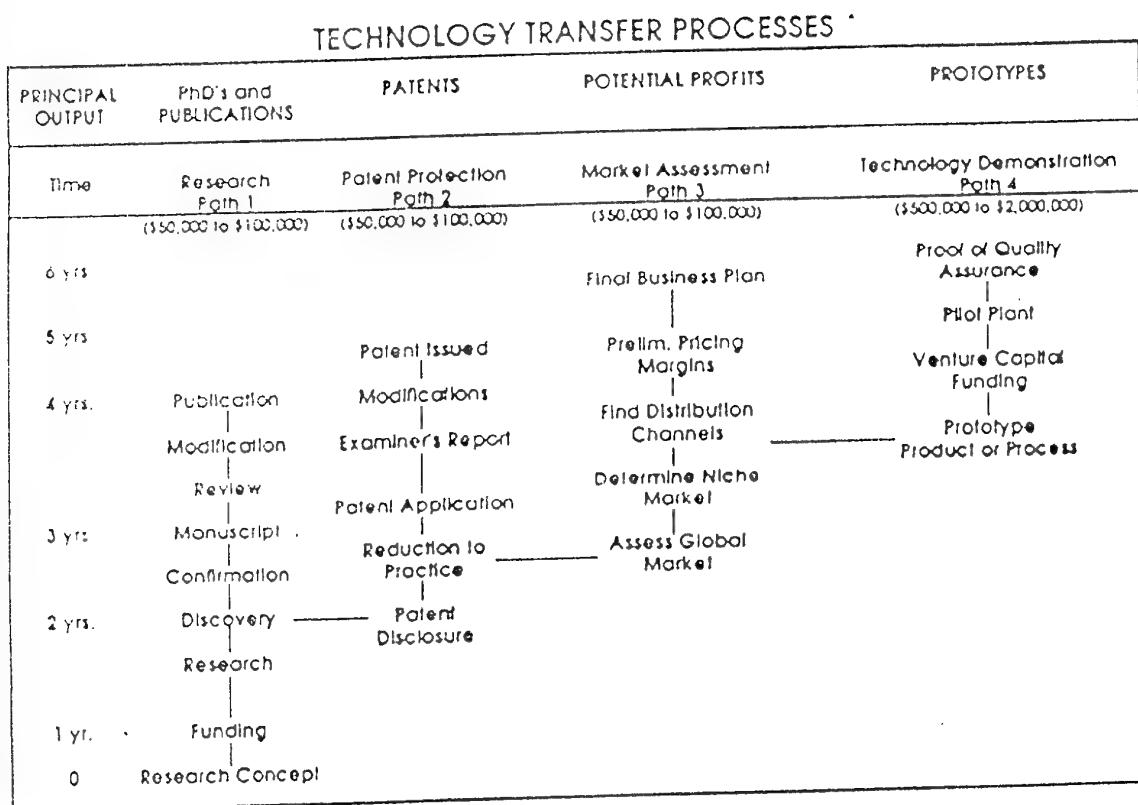
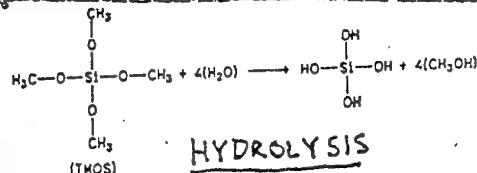


Figure 4. Four primary pathways required for technology transfer.

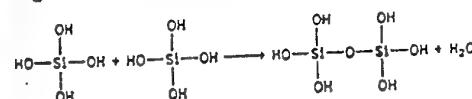
The Sol-Gel Process

L.L. HENCH + J.K. WEST *Chem. Rev. (1990)*, 90, 33-79



HYDROLYSIS

The hydrated silica tetrahedra immediately interact in a condensation reaction forming $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds.



CONDENSATION

Linkage of additional $\equiv\text{Si}-\text{OH}$ tetrahedra occurs as a polycondensation reaction and eventually results in a SiO_2 network.

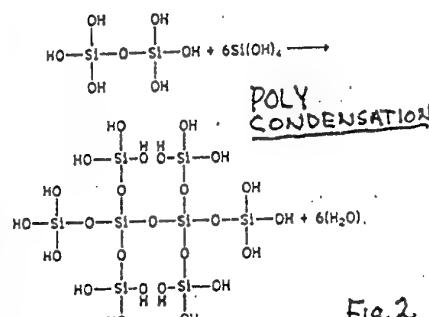


Fig. 2

SOL-GEL PROCESS

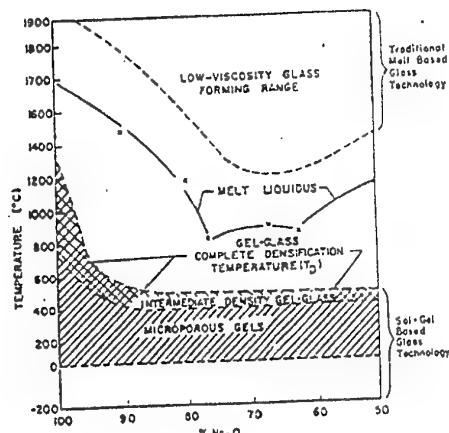


FIG. 1. Thermal compositional processing diagram for the sol-gel-derived $\text{Na}_2\text{O}-\text{SiO}_2$ system.

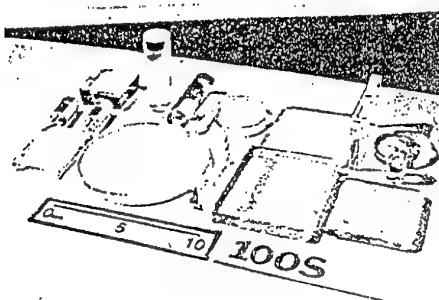
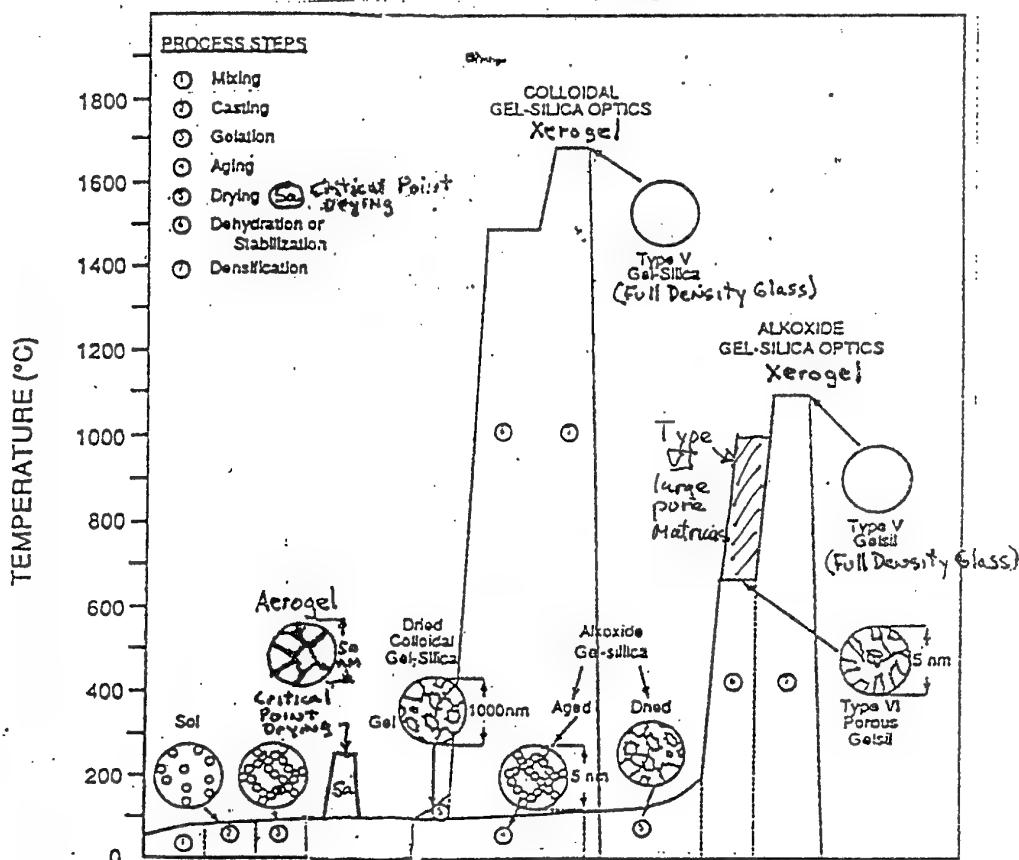


FIG. 4. Silica optical components made with the sol-gel process.



RELATIVE TIME

Figure 3. Processing sequence for sol-gel silica optics.

Present Problems and Future Needs in Biomedical Materials

Larry L. Hench
Professor of Ceramic Materials
Imperial College of Science, Technology and Medicine
University of London

Present Problem: Many patients outlive their prostheses requiring revision surgery.

Reference: *Clinical Performance of Skeletal Prostheses*, L.L. Hench and June Wilson, eds.
Chapman and Hall (1996)

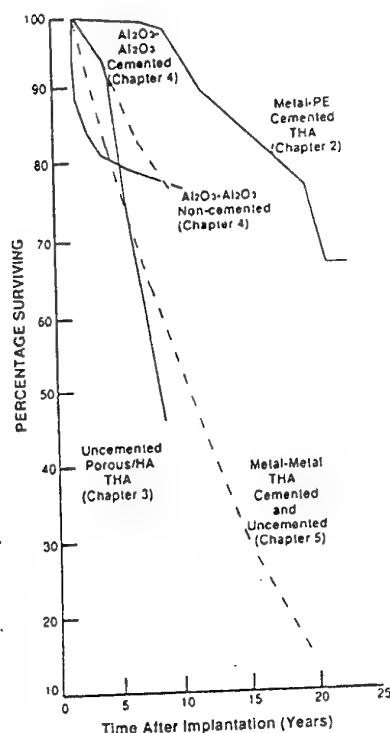


Fig. 16.1 Survivability curves for total hip arthroplasties

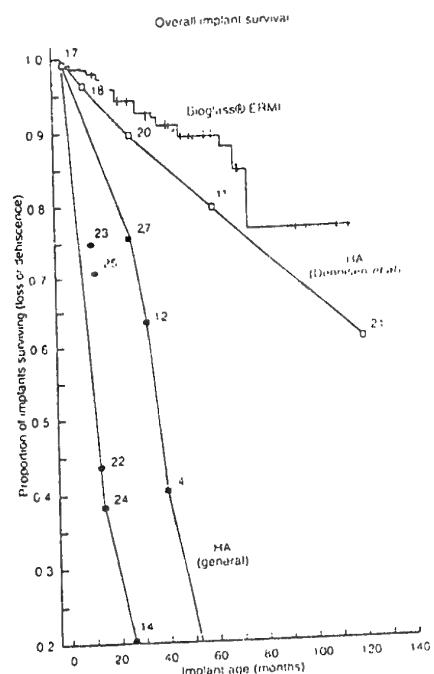
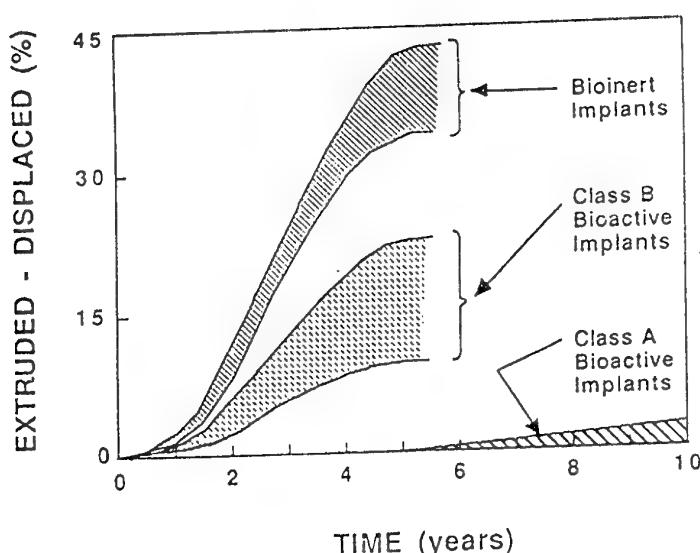


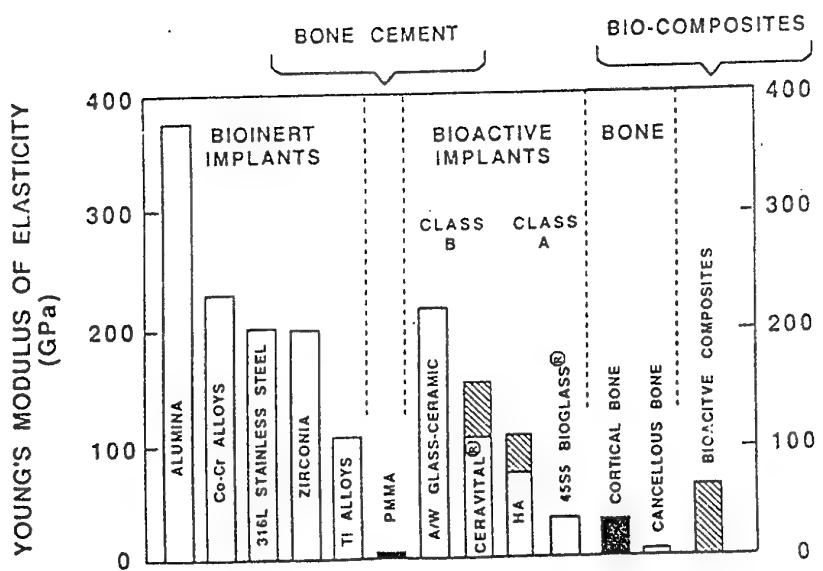
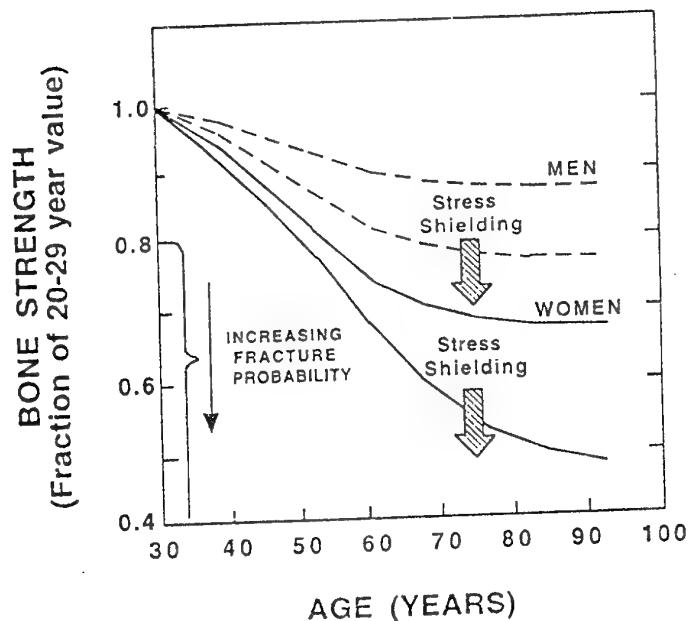
Fig. 15.1 Survivability of alveolar ridge maintenance implants. Numbers correspond to reference citations given in bold

EXTRUSION - DISPLACEMENT RATE vs. TIME
OF IMPLANTATION FOR VARIOUS MIDDLE
EAR OSSICULAR REPLACEMENTS
(data compiled by K. Lobel)



Sources of the Problem:

- 1) Lack of interfacial bonding between implant and tissue.
- 2) Mismatch of elastic modulus of implant and tissue leading to stress shielding and accelerated deterioration of bone.
- 3) Implants are not designed with respect to the progressive deterioration of bone quality of aged patients.



New approaches to the Problem

- 1) Bioactive Composites: PE-HA, PE-Bioglass®, PS-Bioglass®, PPS-Bioglass®
- 2) Tissue Engineering: Hierarchical scaffolds
- 3) Tissue Regeneration: Mitogenic response of osteoblasts
- 4) Molecular modelling and design of biological-implant interactions

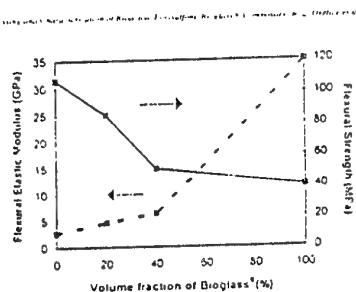
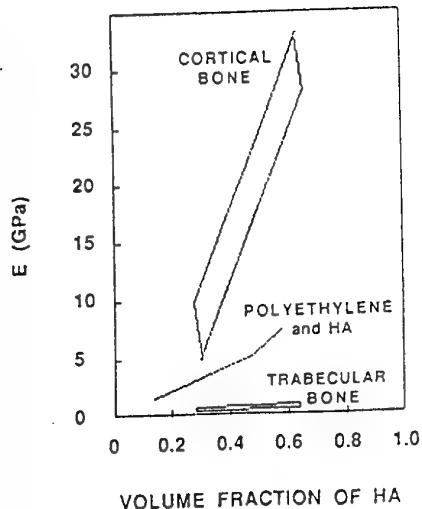
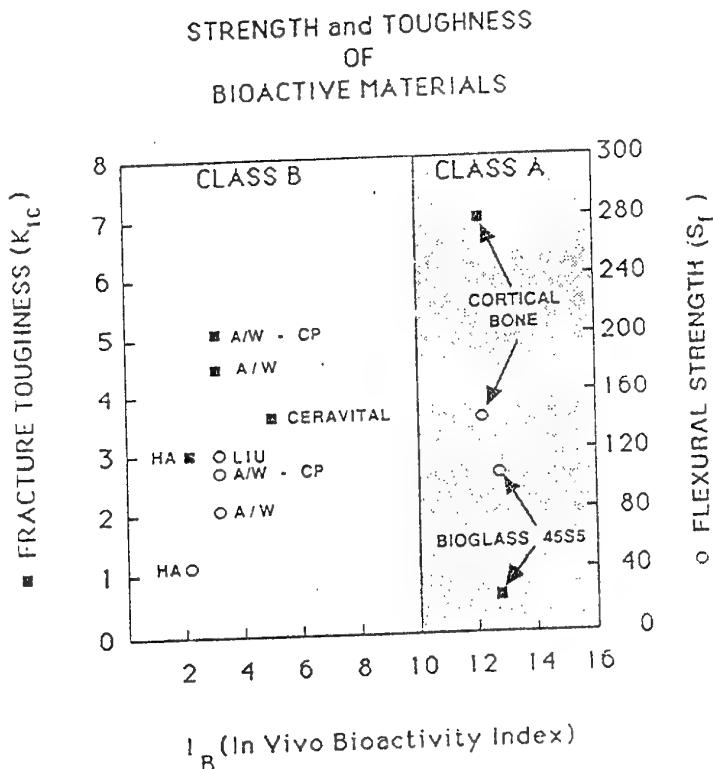
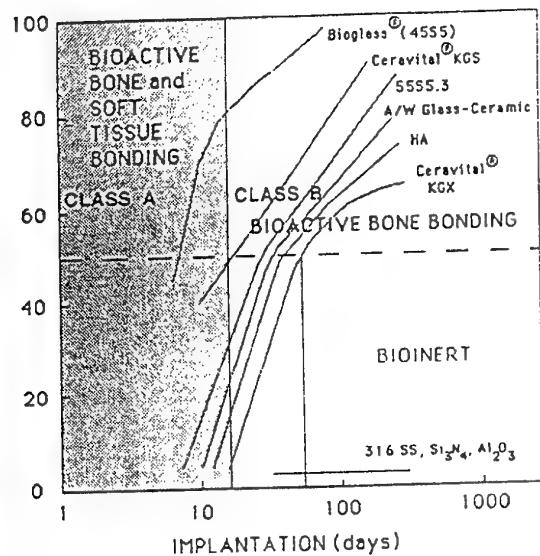


Figure 3. Flexural elastic modulus and stress at failure for polysulfone-Bioglass® composites

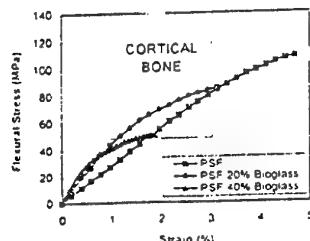
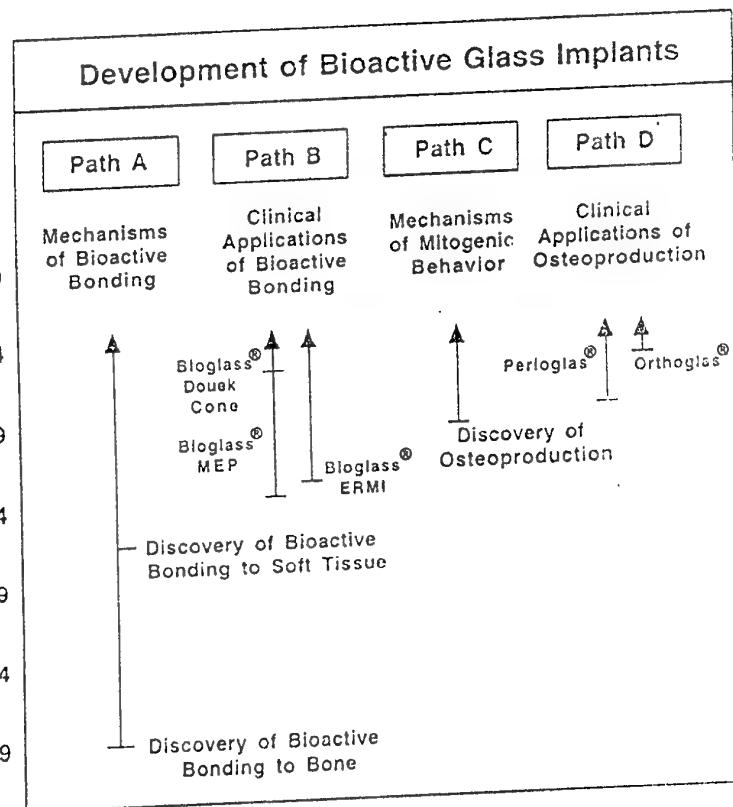
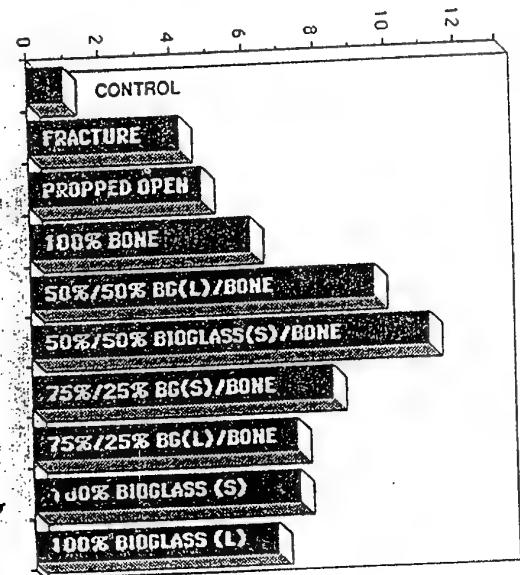


Figure 4. Engineering stress-strain curve for polysulfone-Bioglass composites



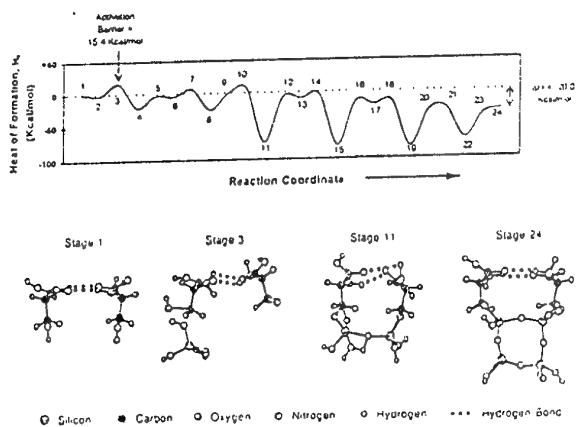
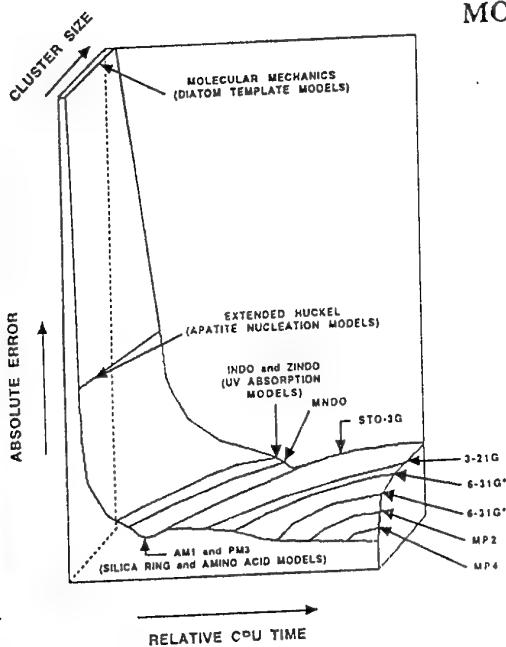
EXTENT OF AUGMENTATION ($\frac{S_A}{S_A + C}$)



SEM image of the same area after 12 weeks. Mature trabecular bone structure has formed between and around the bioglass particles, which show signs of extensive chemical reaction. The particles have apparently served as a scaffolding for regeneration of the normal bone architecture.

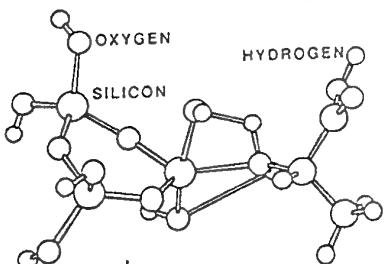
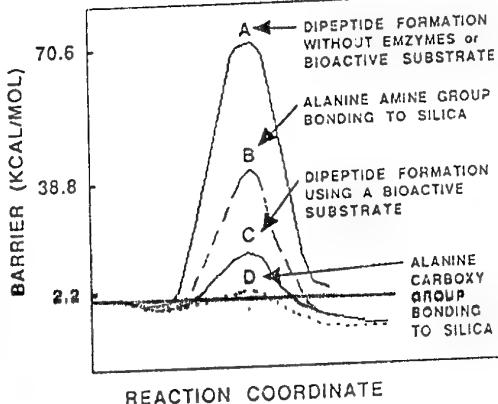
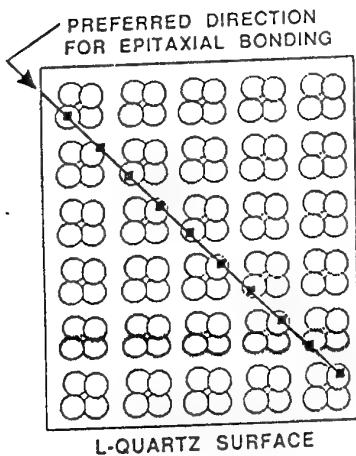


MO Model of the Diatom Frustule: Potential for Biomimetics.

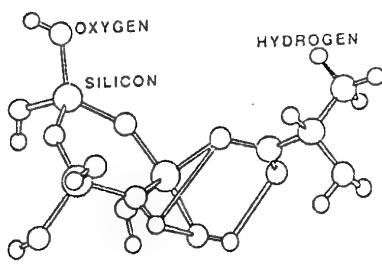


POLY-L-ALANINE BONDS TO REPEAT SITES ON L-QUARTZ (1010) SURFACE IN THE [0111] DIRECTION

AM1 MO MODELS OF SILICA-ALANINE INTERACTIONS PREDICTS BONDING TO OCCUR WITH THE LOWEST BARRIER FOR THE CARBOXY GROUP



[B] TRANSITION STATE DURING SILICA-ALANINE BONDING VIA AMINE GROUP



[D] TRANSITION STATE DURING SILICA-ALANINE BONDING VIA CARBOXY GROUP

*FROM CONCEPT TO COMMERCE:
THE CHALLENGE OF TECHNOLOGY TRANSFER IN MATERIALS
(MRS Bulletin, August 1990, pp. 49-53)*

*Larry L. Hench
Department of Materials Science and Engineering
University of Florida, Gainesville, FL 32611*

TECHNOLOGY TRANSFER PROCESSES

The flowchart illustrates the progression of a project from a Research Concept to Prototypes, with various milestones and financial markers along the way. The timeline is marked by time points from 0 to 6 years, and financial markers in parentheses.

PRINCIPAL OUTPUT

PhD's and PUBLICATIONS	PATENTS	POTENTIAL PROFITS	PROTOTYPES
Research Path 1 (\$50,000 to \$100,000)	Patent Protection Path 2 (\$50,000 to \$100,000)	Market Assessment Path 3 (\$10,000 to \$100,000)	Technology Demonstration Path 4 (\$100,000 to \$2,000,000)

Timeline and Milestones:

- 0 yr.** Research Concept
- 1 yr.** Funding
- 2 yrs.** Discovery → Patent Disclosure
- 3 yrs.** Manuscript Confirmation → Patent Application → Reduction to Practice
- 4 yrs.** Publication → Modification → Review → Patent Issued → Examiners Report → Modifications
- 5 yrs.** Final Business Plan → Prelim. Pricing Margins → Find Distribution Channels → Determine Niche Market → Assess Global Market
- 6 yrs.** Proof of Quality Assurance → Pilot Plant → Venture Capital Funding → Prototype Product or Process

Figure 2. Four primary pathways required for technology transfer.

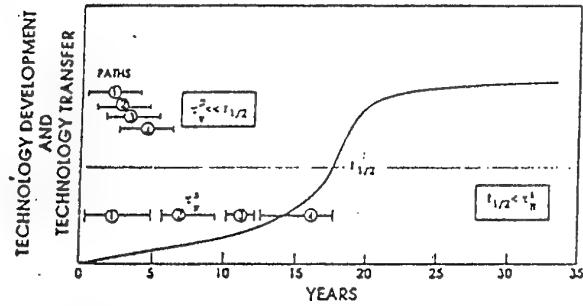


Figure 3. Comparison of parallel vs. serial technology transfer paths with technological development curve.

WORLD-WIDE DISTRIBUTION OF TECHNOLOGY TRANSFER TIMES

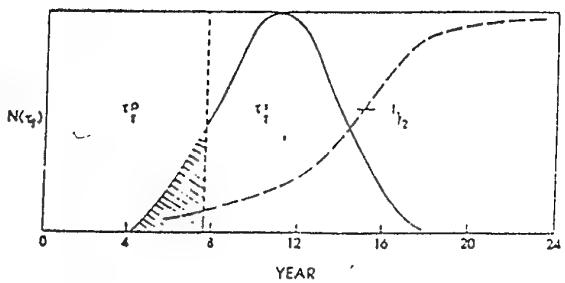


Figure 6. Distribution of technology transfer times compared with technology development curve.

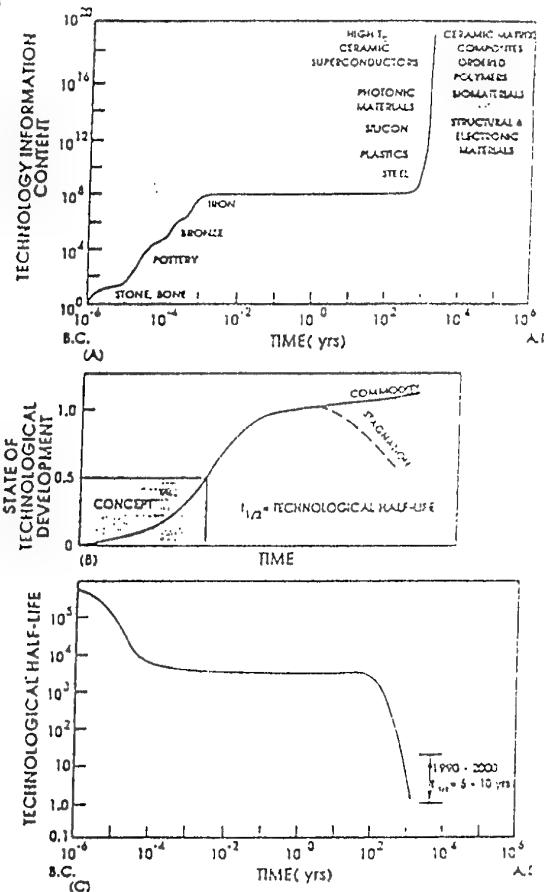


Figure 1. The (a) rapid change in materials technology and (b,c) its effect on technological half-life.

From Concept to Commerce: The Challenge of Technology Transfer in Materials

Larry L. Hench

Introduction

Many millions of dollars are invested annually in materials science research and development in U.S. universities. In the universities and the sponsors, either government or private industry, the enormous incentives for the R&D efforts to become commercial. For private industry a successful development means new or improved products or processes and ultimately more profits. For the government, successful materials development can lead to improved hardware or operations efficiency and lower costs. For a university the payoff may be more than economic. Equally, successful commercial development leads to royalties paid to the universities in the form of the most precious of assets — unrestricted or flexible income. Students and faculty can benefit from the additional income, privately, depending on university policy, and through their departments. However, benefits can also accrue in the form of experience and knowledge gained by participating in the technology transfer process from university to corporation. Students who take part in such efforts gain invaluable experience in writing and defending patent applications, designing and developing prototypes, and they are exposed to economic and legal issues that are seldom taught in the classroom. They become more

valuable graduates. Taking part in a technology transfer case history is a far more effective form of learning than reading about it.

These benefits to a university are offset by a number of potentially negative factors. The space, time, personnel, equipment, and deadline pressures involved in commercialization are often beyond the capabilities of a university program. However, these limitations may not be realized until the effort has begun, and it is costly to stop in mid-stream, as is discussed below.

Thus, university administration and faculty are faced with a dilemma. On one hand, patents, royalties, and commercialization contracts appear to be one of the few solutions to the ever increasing need for new income and especially flexible income at a university. On the other hand, the personnel, experience, or physical resources are seldom available at a university to achieve commercialization efficiently or effectively. The most common solution to the dilemma is an arm's length licensing of the technology. This solution has its own perils and is often difficult to control and enforce. This article examines the relative merits of the alternative routes for commercialization based on the requirements for effective technology transfer. It is based on my personal experience with the commercialization of

several medical, dental, optical, and electronic products,¹ combined with consulting experiences and discussions on business start-up efforts of various faculty and venture capital friends.

Rate of Technological Change

One of the major difficulties faced today in commercializing new technology is the accelerated rate of technology change.

Man's progress is often measured by technological change. These steps, as shown in Figure 1a, are usually marked by changes in materials. From pre-history to the present day, the information content embodied within each new class of material has dramatically increased. The knowledge required to control fire and drafts and clay to make earthenware pottery was many times greater than that used to make implements from natural materials such as bone, wood, or flint. As ceramics and manmade materials were born, mankind was changed forever.

This was the seminal change of civilization. The birth of ceramics was immensely more significant than just having better bowls, jars, and pots. It was the first change leading to man's control over nature rather than accepting living with nature. The irreversible change of clay into ceramics, or natural into unnatural, thus had profound philosophical implications.

The knowledge necessary to win, purify, and alloy metals built progressively upon that developed by the early potter and led to the Bronze Age and Iron Age. Each age, thereafter, built progressively upon the earlier until stagnation in western civilizations occurred during the Middle and Dark Ages. However, following the Renaissance and the onset of the Age of Science, the knowledge content associated with the development of new materials increased at an exponential rate or more (Figure 1).¹⁴

Technological Half-Life

An important consequence of this rapid increase in the rate of change is an ever decreasing technological half-life for new developments (Figures 1b and 1c). At one time, advances in new materials might have lasted for thousands, or at least hundreds, of years. Today, the life span of growth of a new development, from concept to production through rapid expansion and then to maturity and the slow growth of a commodity (Figure 1b), is measured in decades.

By the 21st century, a technological half-life may only be a few years or less. Many fields of materials are already far

past their technological half-lives. Glass containers, structural clay products, whitewares, refractories, and enamels are all examples of ceramic industries where growth seldom exceeds the growth in the GNP, if at all. Ferrous metals, copper, etc. are also at the maturation end of their technological lifetimes. For some materials, stagnation has set in and the growth curve has a negative slope. The technological half-life for these products was in the range of 30 to 40 years. Most of the R&D efforts in these fields past their technological half-life consists primarily of the small evolutionary steps required to just maintain their positions as slow-growth commodities.

Materials science, in the broadest sense, has been equally seminal in the birth of this technological explosion as it was in the birth of man's first technology. The rapid rate of change in information content of new materials parallels the rapid rate of information transfer within society. The two rates are interconnected and lead to the autocatalytic explosion of technological development shown in Figure 1c.

Without the technology of high performance insulation and dielectric isolation, microencapsulation and packaging, high storage capacitors, ultrahigh purity crystal growth, chemically doped semiconductors and many more, there would be no microelectronics or information processing field today. The next major expansion in microelectronics is very likely to involve high T_c ceramic superconductors, which require the application of advanced ceramic processing technology to produce useful products. Recent developments in high temperature ceramic matrix composites and transformation-toughened ceramics indicates that this field is at the threshold of revolutionizing high temperature structural applications of materials. Carbon-carbon composites are already making a major impact on aircraft structure and turbine design. The development of reactive ceramics, glasses and glass-ceramics and molecular control of polymer surfaces has begun to revolutionize materials and many areas of medical and dental treatment. Likewise, recent advances in solid state lasers, sol-gel derived optics, quantum confinement, and nonlinear optical materials are beginning to yield important advances in optical based communications and information processing systems. Thus, the fields of superconducting materials, ceramic matrix composites, toughened structural ceramics, multi-

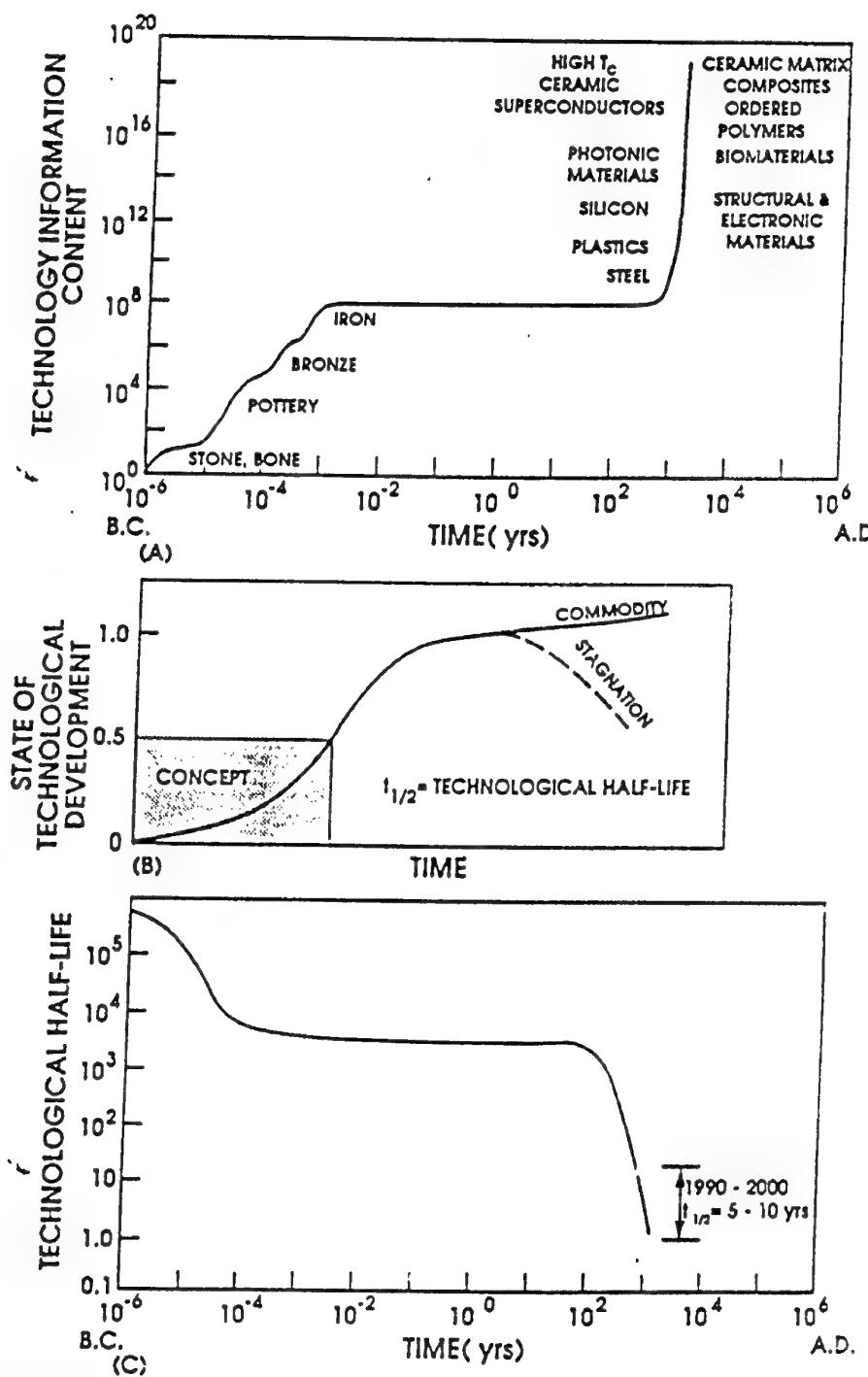


Figure 1. The (a) rapid change in materials technology and (b,c) its effect on technological half-life.

functional polymers, biomaterials, and photonic materials are all at the earliest stages of their technological lifetimes. Thus $t < T_{1/2}$ for these new materials.

However, the rapidly decreasing value of $T_{1/2}$, Figure 1c, for all technological developments makes it progressively more difficult to project a technological

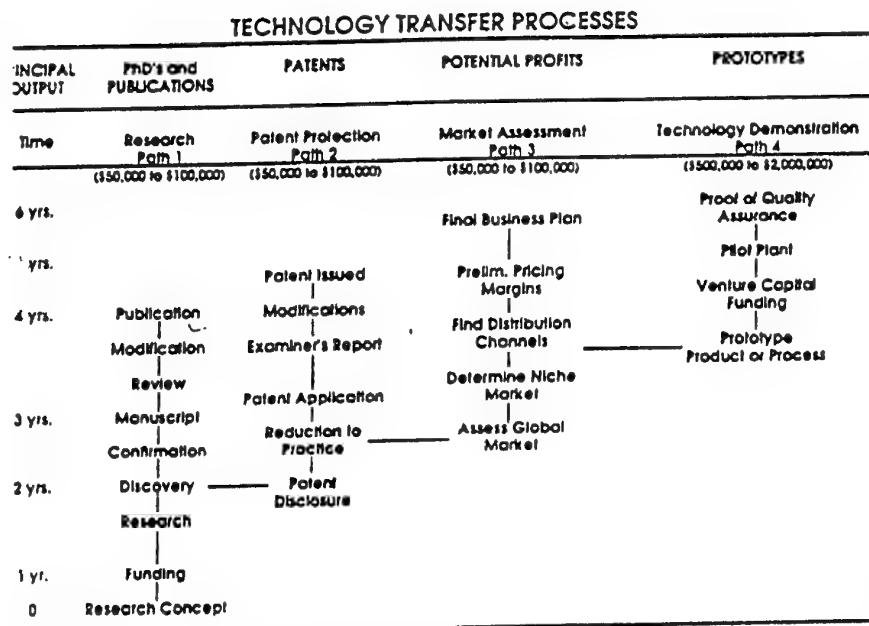


Figure 2. Four primary pathways required for technology transfer.

life for any singular new development, even ones as exciting as those cited above.

Technological Transfer

The uncertainties of technology transfer make it difficult for materials science and engineering programs to meet the challenge of rapid change within a university. Technology transfer is often considered to be like death and taxes, inevitable. In fact, the technology transfer process is both long and complex. Figure 2 summarizes the many steps involved in bringing a research idea from concept to commercialization. There are four primary paths in achieving technology transfer, each with a distinctly different principal output:

Path	Output
Research	PhDs and Publications
Patent Protection	Patents
Market Assessment	Profit Potential
Technology Demonstration	Prototypes

four paths must occur in order for a concept to become a commercial success, i.e., to become a product which can be produced and sold in the marketplace with a reasonable return on investment. Each technology transfer path has a time line which is governed by the

serial sequence of steps indicated in Figure 2.

Although a specific length of time is indicated for the steps shown in Figure 2, in reality the distribution of times is unique for a given product and organization. However, the time lines shown in Figure 2 tend to skew toward the short end of the distribution and so can be used as a good measure of effective technology transfer. If time increments are longer than those shown, there is likely to be a problem somewhere in the organization.

In practice, the length of time for each of the four paths shown in Figure 2 is close to being optimal. It is seldom possible to decrease the length of time required for either the research, patent protection, market assessment, or technology demonstration phases of a new product, assuming that the product involves substantially new technology. Improvements in previously existing processing or products take perhaps a third less time in the technology demonstration phase because the pilot plant facilities already exist. However, the time lines for R&D and patent protection are nearly invariant, regardless of the level of innovation being pursued. Also, experience shows that it is seldom possible to short-circuit any of the individual steps in Figure 2 without suffering expensive delays later.

Figure 2 shows technology transfer

as four parallel paths. It is optimal to pursue all four paths in parallel, rather than in sequence, for several reasons: (1) shorter cumulative time, (2) feedback of information between paths, (3) maintenance of momentum, and (4) lower total cost.

If it is possible to pursue the four technology transfer paths in parallel, as shown in Figure 2, then the cumulative time for a successful technology transfer process is approximately six years. However, if it is necessary to complete each path prior to commencing the next, the cumulative time is more than doubled to 12 years. Often this is the case because the costs associated with patent protection and technology demonstration are usually considerably larger than research costs. Consequently, new layers of management become involved in the decision making process as one moves from Path 1 > 2 > 3 > 4. Since the project costs of Paths 2-4 are substantially higher than usually budgeted in universities, the time required to evaluate the project and also the number of people required to evaluate go up proportionally. The probability of approval goes down proportionally.

A combination of factors often leads to a long serial technology transfer process. The major impedance step in the serial process is the transfer from Path 3 > 4. The level of financial commitment goes up by a factor of 10 at this point. However, cost is not the only barrier in moving from Path 3 > 4. Personnel, management, and facilities are equally important factors.

In order to achieve a demonstration of the technology (Path 4) it is essential to create a team composed of the scientist(s) who originated the discovery, engineers capable of scaling-up the technology and experienced in designing the requisite equipment, along with technical staff, and management. Experience, skills, attitudes, responsibilities, and temperaments differ greatly among such a team. Consequently, considerable time can be invested in achieving an acceptable schedule, plan of action, budget, and commitment to "make it work."

Most of the time the technology will not work in the demonstration scale without a number of trials. Consequently, feedback of information from the technology demonstration team to the science team and vice versa, i.e., Paths 1 > 4, is essential. However, by this time creative scientific personnel will have already moved on to other interests and are not enthused about returning to an

"old" project when problems arise. The net effect is a lengthening of Path 4. These difficulties can arise whether the technology transfer effort occurs within the university or with an "arm's length" licensing agreement between the university and a corporation.

In most cases the funds to pursue a Technology Demonstration project will not be approved without completion of a marketing and commercialization study, Path 3. The marketing analysis will attempt to project: cost/benefit ratios, capital required, size of market, time to reach the market, percentage of market penetration, competitive position of the new technology, lead times over the competition, profit margins, effect on existing corporate products, etc. Most university science and engineering departments do not have the staff or experience to make this analysis.

The greater the advance of the new technology, the more difficult it is to make these marketing and commercialization assessments. Therefore, the better the technology the greater is the risk and the longer is the time required to pass judgment that it should be supported to enter Path 4, and become a Technology Demonstration Program. One dominant mode of dealing with a high risk decision is to postpone it. Again, the effect is to lengthen the initiation of Path 4 and the overall technology transfer time line.

Thus, there are two primary difficulties in pursuing Paths 2, 3, and 4 entirely in parallel: (1) the 5 to 10 increase in cost of moving from prototypes to pilot-plant scale operations, and (2) the need to complete market assessments before large budgets can be approved. Consequently, the staggered parallel paths ($2 > 3 > 4$) shown in Figure 2 are required by economic realities.

The cumulative time for a staggered parallel technology transfer program ($t_{n,1}$) is approximately six years; for a serial technology transfer program ($t_{n,2}$), approximately 12 years. It requires a very high level of organizational efficiency and substantially greater risk to reduce these figures to shorter times. It is extraordinarily easy for the time lines to lengthen.

The Problem

Comparing Figures 1 and 2 identifies a serious problem. For a given field, as $T_{1/2}$ decreases it approaches $t_{n,2}$. Consequently, when $T_{1/2} \leq t_{n,2}$, a development program will have reached its technological half-life before it is even out of the pilot plant stage. This is indeed pos-

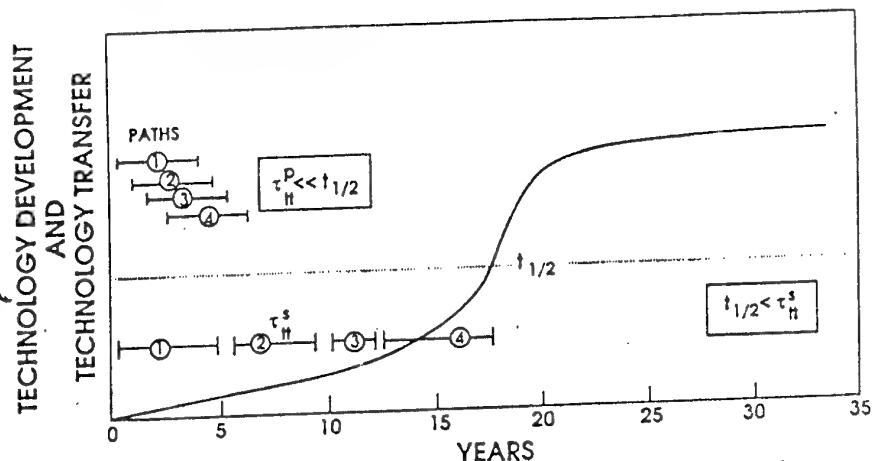


Figure 3. Comparison of parallel vs. serial technology transfer paths with technological development curve.

WORLD-WIDE DISTRIBUTION OF TECHNOLOGY TRANSFER TIMES

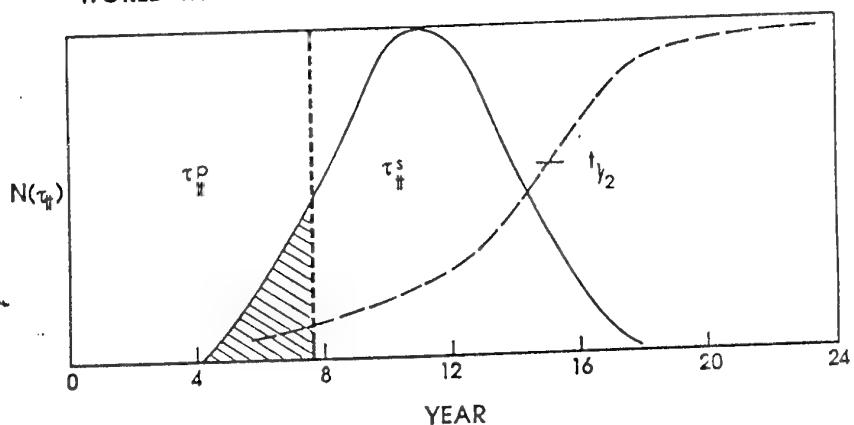


Figure 4. Distribution of technology transfer times compared with technology development curve.

sible because of two factors: (1) There are an exponentially growing number of alternative developments being pursued simultaneously; and (2) there is a distribution of $t_{n,2}$ for each alternative. This competitive situation is illustrated in Figure 3, where the time curves for serial $t_{n,2}$ and staggered parallel $t_{n,1}$ are compared with the technology development curve.

Consequently, development alternatives with a short $t_{n,2}$ will enter production and rapidly achieve market dominance while competitive developments are still within Paths 3 and 4 in the technology transfer process.

As indicated previously, any given

technology transfer program is in fact competing with many other programs worldwide. Each program will have a characteristic value of $t_{n,2}$. The distribution of $t_{n,2}$ is compared in Figure 4 with the technology development curve. It is apparent that only the programs skewed to the short end of the distribution will share in the rapid growth and rapid return on investment.

Thus, efficiency of technology transfer and speed of response to new developments become the major factors for commercial success.

This is a dramatic change from the

past (see Figure 1a) when proximity or quality of resources, size or skill of manpower pool, cost of energy, size, proximity to markets, availability of capital, or government subsidy were the dominant factors for success of a business.¹⁻³

The materials industry in the United States and Europe receives fairly poor marks in recognizing and responding to this challenge of rapid change. There is relatively little effort in evidence that the traditional materials industry is accelerating technology transfer processes. The emphasis remains on large plants with large capital investment and very slow response times to change. The investment in basic processing R&D is far lower than required to maintain parity in rapidly developing technical areas. There is in general too little freedom, imagination, and flexibility in R&D directions.

The Solution (Perhaps)

Most importantly, there are very few long-range R&D and technology transfer collaborations between materials firms, universities, and the U.S. government. A few such programs have been organized but in general they do not have sufficient funding or personnel or industrial commitment to have a major impact on this problem.

However, collaborative programs are a step in the right direction. Existing programs should be doubled or tripled in size and a minimum of 5 to 10 new advanced materials R&D programs should be established with interdisciplinary faculty, staff, and students involved. However, I submit that for such interdisciplinary programs to be successful they must be organized to pursue all four technology transfer paths in an optimal staggered parallel manner.

This requires that budgets be approved with sufficient funds to pursue Paths 2, 3, and 4 without long and costly delays. It also means that such programs should have market analysis teams associated with the program from the start in order to minimize the Path 2 > 4 delays. The critical size and budget for such an integrated enterprise is a factor of five larger than most collaborative programs in existence. As a result, most so-called collaborations seldom, if ever, move past (1 > 2) in their payoffs. Path 3 is seldom organized and Path 4 is commonly pursued through licensing arrangements with little incentive to utilize university expertise. The "Not Invented Here" syndrome stifles progress even if there are corporate benefits to move quickly through Path 4.

Conclusion

In the age of ever decreasing technological half-lives, it is extremely important to utilize all available resources to bring about the rapid commercial utilization of technology developed in universities. If the United States is determined to compete in the worldwide market for high-tech products, then it must realize the full benefits of collaborative means of product development.

This requires recognizing the economic requirements and risks of technology demonstration projects. It also requires organizing university programs so as to share the risks among corporations and/or large capital firms. The cost of sharing these risks is to decrease the potential financial returns on the technology to the university. The cost of not sharing the risks, or delaying the decision, is to lose the competitive race to those organizations that are organized to do so. "Time is money" is a proven axiom in the business world. It

is often a foreign concept in a university. Only when universities recognize that rapid time lines for technology transfer are as valuable as the technology itself will we be able to compete effectively in the worldwide technology race. The prognosis at present is doubtful.

Acknowledgments

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BIOACTIVE MEDICAL AND DENTAL MATERIALS

Lecture 1: CLINICAL NEEDS AND TYPES OF BIOMATERIALS

Aging results in a progressive loss of the mass and strength of bone (Figure 1) which leads to fracture of hips, long bones and collapse of vertebrae. Biomaterials in the form of implants or devices are used to repair, augment or replace diseased, damaged or aged bones and teeth.

The materials historically developed for implants are corrosion resistant but elicit a non adherent fibrous capsule which isolates the material from the living tissue. These materials must be fixed in place by either a self-curing polymer, polymethylmethacrylate, PMMA, (cement fixation) or by mechanical interlocking (morphological fixation) or by porous ingrowth of bone (biological fixation).

In contrast, bioactive materials form a chemically bonded interface with living tissues. Bioactive glasses composed of $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ have the highest rates of bioactive bonding and develop a bond with bone and soft connective tissues. The bond is between collagen fibrils and a layer of biologically grown hydroxycarbonate apatite that forms on the surface of the implant. These Class A bioactive implants stimulate the proliferation of new bone in a process termed osteoproduction. Synthetic hydroxyapatite (HA) has an intermediate level of bioactivity and bonds only to bone by osteoconduction, it is a Class B bioactive material.

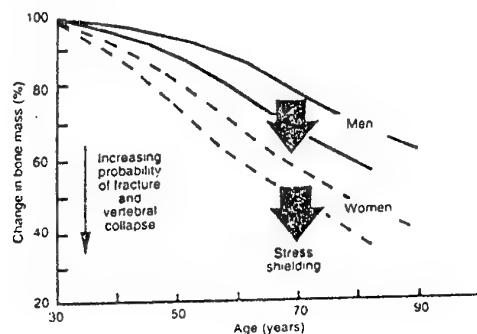


Fig. 1.1 Effect of age on bone mass. Data derived from G.R. Mundy (1994) *Nature* 367, 216-17.

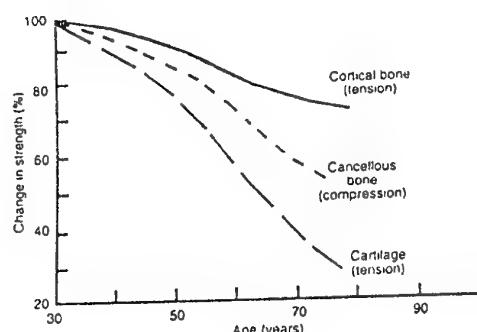


Fig. 1.2 Effect of age on strength of bone and cartilage. Data from H. Yamada (1970). *Strength of Biological Materials*. Williams and Wilkins, Baltimore, MD.

Lecture 2 : TISSUES AND THEIR REACTION TO IMPLANTS

There are four main types of tissue in the body, epithelium, muscle, nerve and connective tissue. All organs consist of a combination of these tissues in varying proportions.

When a tissue or an organ is injured, which can be the result of infection, disease, an accident or deliberate surgical intervention, the body responds with a series of events to repair the damage and restore the tissue to normal. These processes are those of inflammation and repair and, under most circumstances, the repaired tissue is virtually indistinguishable from adjacent undamaged areas.

The situation is rather different when an implant is placed in the repairing tissue. The implant material controls the rate and nature of the repair and such effects depend on the properties, both chemical and mechanical, of the material as well as its size and shape.

Implant materials can be divided into three main types used in surgery,

- a) inert, such as silicone rubber.
- b) degradable, as used for some sutures.
- c) bioactive, such as Bioglass® and similar ceramics.

These different materials produce different effects on tissues which must be understood and more importantly, controlled, before a material can be selected for a specific application.

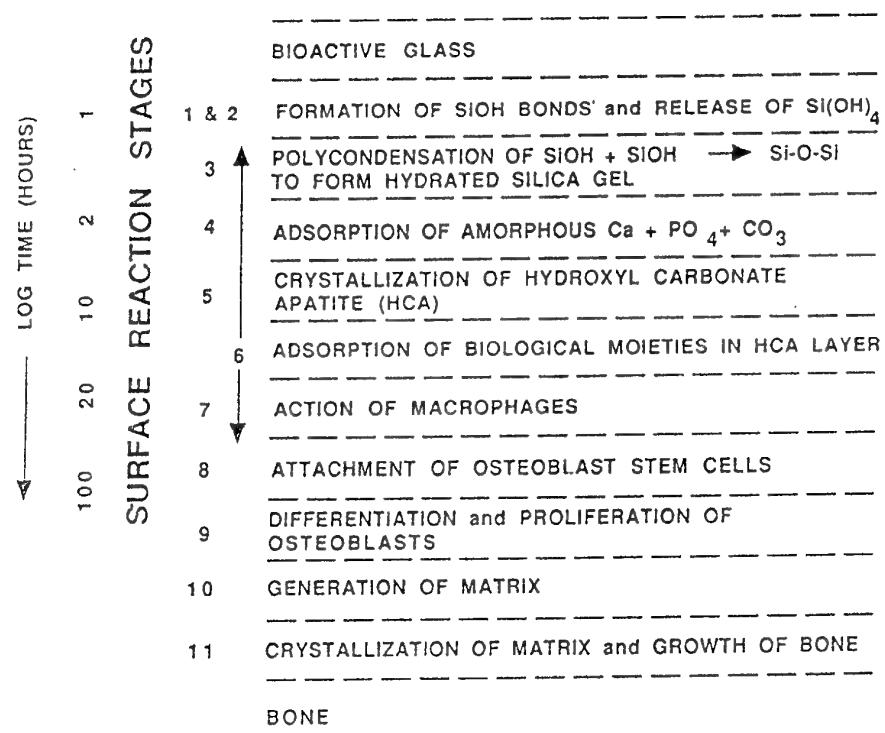
Lecture 3: PRINCIPLES OF BIOACTIVE BONDING

There are 11 stages of reaction involved in forming a bond between a Class A bioactive glass implant and bone (Figure 1). The first two stages, ion exchange, and network dissolution occur very rapidly when the glass is in contact with body fluids. The result of Stages 1 and 2 is release of soluble Si, Ca, and P ions to the body fluids. Stage 3 is polymerization of the large concentration of silanols (Si-OH) ions created during stages 1 and 2 to form a hydrated silica gel surface. The high surface area of the silica gel chelates Ca and P ions to form very rapidly an amorphous Ca-P rich layer (Stage 4) which rapidly crystallizes to become a biologically active hydroxycarbonate apatite (HCA) layer (Stage 5).

Biological moieties, such as growth factors, adsorb and desorb from the silica gel and HCA layers (Stage 6). The proteins affect the extent of time and behaviour of macrophages which are initially present in any implant site (Stage 7). The bioactive surface also enhances the attachment, differentiation, and proliferation of osteoblast stem cells which leads to a rapid proliferation of new bone and mineralization of the bone matrix (Stages 8-11).

Bioactive glasses can be used as particulates which leads to rapid regeneration of trabecular bone or as bulk materials which rapidly form a bond to either cortical or trabecular bone. The bioactive glasses can also be used as a bioactive phase in a composite with a polymer matrix which yields moduli of elasticity equivalent to natural bone. Bioactive composites offer the important advantage of avoiding stress shielding of bone while maintaining a biological bond at their interface with tissues.

SEQUENCE OF INTERFACIAL REACTIONS INVOLVED IN FORMING A BOND BETWEEN TISSUE AND BIOACTIVE GLASS



Lecture 4: MEDICAL AND DENTAL APPLICATIONS OF BIOACTIVE IMPLANTS

In the last 15 years Bioglass® has been used in an increasing number of clinical situations.

In maxillofacial and otolaryngological applications it has been used as a solid device to treat conductive hearing loss due to *otitis media*, trauma or congenital defects. It is a critical component of a cochlear implant which can help those whose deafness is the result of nerve damage. As a particulate, it has been used to fill bony defects in the mastoid and the orbit, and to mobilise a paralysed vocal cord.

In urological applications it has been used, in an injectable form, to treat urinary incompetence secondary to *spina bifida* and has promise as a treatment for vesico-ureteral reflux.

In orthopaedic surgery the particulate has been used to supplement autologous bone (or to replace it) as a material to repair bony defects in the spine, cranium or long bones.

In dentistry the particulate is the material of choice for repair of periodontal defects, and filling of dental cysts. Maintenance of the alveolar bone is achieved with solid root-form implants placed in an edentulous ridge.

The unique ability of Bioglass® to bond to both hard and soft tissue, as and where required, is what makes it suitable for so many diverse clinical applications.

There has never been a report of an adverse effect attributable to the material at any time during its development.

Infra-Red transmitting glasses

Lecture I : the glass forming systems

The glass science and technology has been in the past almost totally dominated by glass forming materials such as the oxides SiO_2 , P_2O_5 , B_2O_3 , etc...

Despite their excellent glass forming ability, those materials suffer from a limited transmission in the infra-red part of the spectrum.

Oxide glasses have an IR cut-off in the $3 \mu\text{m}$ region and consequently they are totally opaque in the two strategic atmospheric windows located in the regions $3 - 5 \mu\text{m}$ and $9 - 12 \mu\text{m}$.

The rule for preparing an IR glass is to combine heavy atoms having a chemical bond which is strong enough in order to ensure the stability of the vitreous materials.

Indeed the two factors which limit the interest of IR glasses are :

- 1) a low glass transition temperature T_g leading to weak thermomechanical properties,
- 2) a bad chemical durability specially in front of moisture or water corrosion.

With respect to those two parameters, it can be considered that the majority of the chlorides, bromides or iodides based glasses described in the litterature have only a pure academic interest.

The chalcogens based materials are the most promising IR vitreous materials sometimes combined with halogen.

The glass-forming ability of chalcogen based glasses can be discussed by reference to their structure and the concept of glass to crystal competition : for example 1D, 2D and 3D framework can be found in the chemistry of S, Se, Te based glasses. Therefore, an objective examination of the field indicates that the number of technically acceptable IR glasses are very limited.

Infra-Red transmitting glasses

Lecture II : the optical properties of IR glasses

Most of the efforts devoted to IR glasses have been motivated by three reasons :

- 1) The need of vitreous materials covering the IR atmosphere windows 3 - 5 μm and 8 - 12 μm ,
- 2) The potentiality of developing materials having ultra low optical loss for telecommunication links or laser power transmission,
- 3) The development of active glasses doped by lanthanide for example, for efficient laser or amplification applications : this aspect will be developed in lecture IV.

The search of material having a good transmission in the UV is very active, but usually this function is not covered by IR glasses and SiO_2 itself is an excellent UV glass. On the other hand, heavy atoms glasses are specially interesting because of the dependance of the IR cut-off position as a function of the atomic weights. For instance, the fluoride glasses transmit the light from 0,3 μm to the ultimate limit of 8 μm : consequently, they are useful glasses for the visible region and the first 3 - 5 μm window used in some night vision system. All the heavy halides such as chloride, bromide, iodide glasses have a very weak durability and have a limited interest. The chalcogen based materials due to the presence of a non-bonding level associated to lone pair electrons have a small band-gap and the edge is usually in the near IR rendering those materials black. Their poor transmission in the visible is compensated by an IR cut off shifted towards long wavelength sometimes 20 μm . Their dual capability in the two atmospheric windows is ideal for night vision devices, such as IR cameras, thermal sensors, etc... The advantage of the glassy state is obvious due to the possibility of shaping the material by moulding, fibering, extending technics, extruding...

In combining band gap and IR absorption, it can be demonstrated by the theory that very low absorption is expected in the middle of the so called V shape curve. For instance, optical loss as low as 10⁻² dB/km is expected for fluoride glasses. As a matter of fact, extrinsic losses due to defects and impurities forbid to reach this ultra-high transparency.

Infra-Red transmitting glasses

Lecture IV : Rare-earth doped glasses : optical amplifier, fiber laser

Passive functions such as IR waveguiding as described in lecture III, as well as development of new IR optics for camera or night vision systems are the most obvious applications of non-conventional glasses. Nevertheless, these vitreous materials can also be very interesting hosts for rare-earth dopants leading to active functions such as laser emissions or optical amplifications.

Rare-earth, when properly activated by UV, visible or near IR photons can produce fluorescence light either by the traditional process of photons relaxation from an excited state but also by more complex mechanism involving photon addition and up-conversion or excited state absorption phenomena.

The IR glasses have a great superiority to the silica glass due to their low phonon energy rendering the fluorescence emission much more efficient in weakening the part due to phonon relaxation, in other words heat dissipation.

Rare-earth ions are not accepted by all the IR glasses, specially those having a giant molecule character. Therefore, several matrices are excellent hosts, for instance : ZrF₄-based glasses (ZBLAN) where the rare-earth play the role of glass former, or Ga₂S₃-based glass, Ga₂S₃ when the rare earth is a modifier ion.

The most spectacular results in the last decade have been obtained when the IR glass is designed as a core-clad single-mode fiber. This optical configuration results in a high confinement of excited light in the core which contains the doping ions.

Laser operation are obtained for rather low threshold and more than 50 lasing wavelengths have been produced, lying from the blue-UV due to up-conversion phenomena to mid IR for instance $\lambda = 3,9 \mu\text{m}$ with Ho³⁺.

Optical amplification for regenerating the optical telecommunication signal is also an emerging and fascinating technology. Two wavelengths can be used in the telecom windows $\lambda = 1,3$ and $1,5 \mu\text{m}$. For the latter λ , Er³⁺ in silica is totally adequate, while for the former λ , only the solution of Pr³⁺ in low phonon glasses such fluoride glasses have permitted the development of an industrial amplifier.

Infra-Red transmitting glasses

Lecture V : Infra-Red glasses for integrated optics

Guiding the light, in many complex optical configurations at the surface of a glass sample, have been the subject of intensive investigations during the last two decades. Beam splitters, multiplexers, interferometers, sensors have been developed from the concept of planar waveguiding due to a surface gradient index structure produced by ionic exchange on a SiO_2 based glass.

The interest of these guiding structures for passive or active applications is limited by the intrinsic phonon energy of the matrix which is in the range of $W_p = 1200 \text{ cm}^{-2}$. In order to produce channel waveguide transparent in the visible to 8μ region, and to develop efficient microlaser or other active devices, fluoride glasses have been selected as the most reliable vitreous matrix for gradient index structure fabrication.

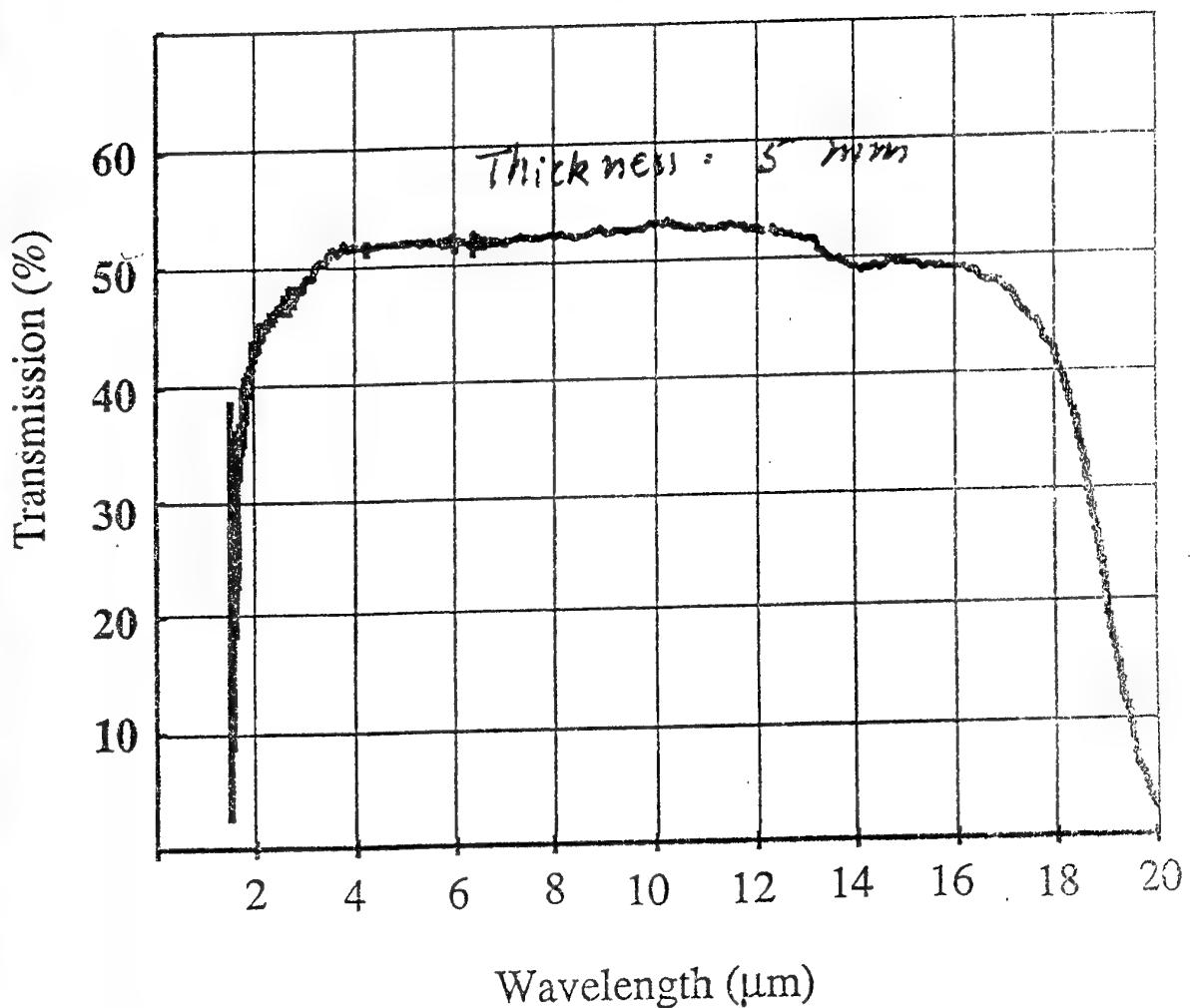
The glass substrate is either a ZrF_4 based glass or an InF_3 glass and the technology to produce a variation of refractive index at the surface while keeping good optical transparency is the ionic exchange. Two methods have been developed :

- 1) the first one consists in a cationic exchange between a Na rich fluoride glasses and a Li containing organic melt such as the palmitate salts,
- 2) the second one consists in modifying the anion composition by substitution of F^- by OH^- or OD^- in treating the glass surface by a controled atmosphere of water vapour.

The analysis of the propagation modes in the planar waveguide is checked by M lines method. Photolithographic processes can be applied with some restrictions to produced channel waveguides. Single mode propagation have been observed by near field measurements indicating an excellent light confinement in the waveguides. This technology open the way to the development of many micro-optics devices such as evanescent wave sensors, microlasers or micro-amplifiers when the waveguides is activated by rare-earth.

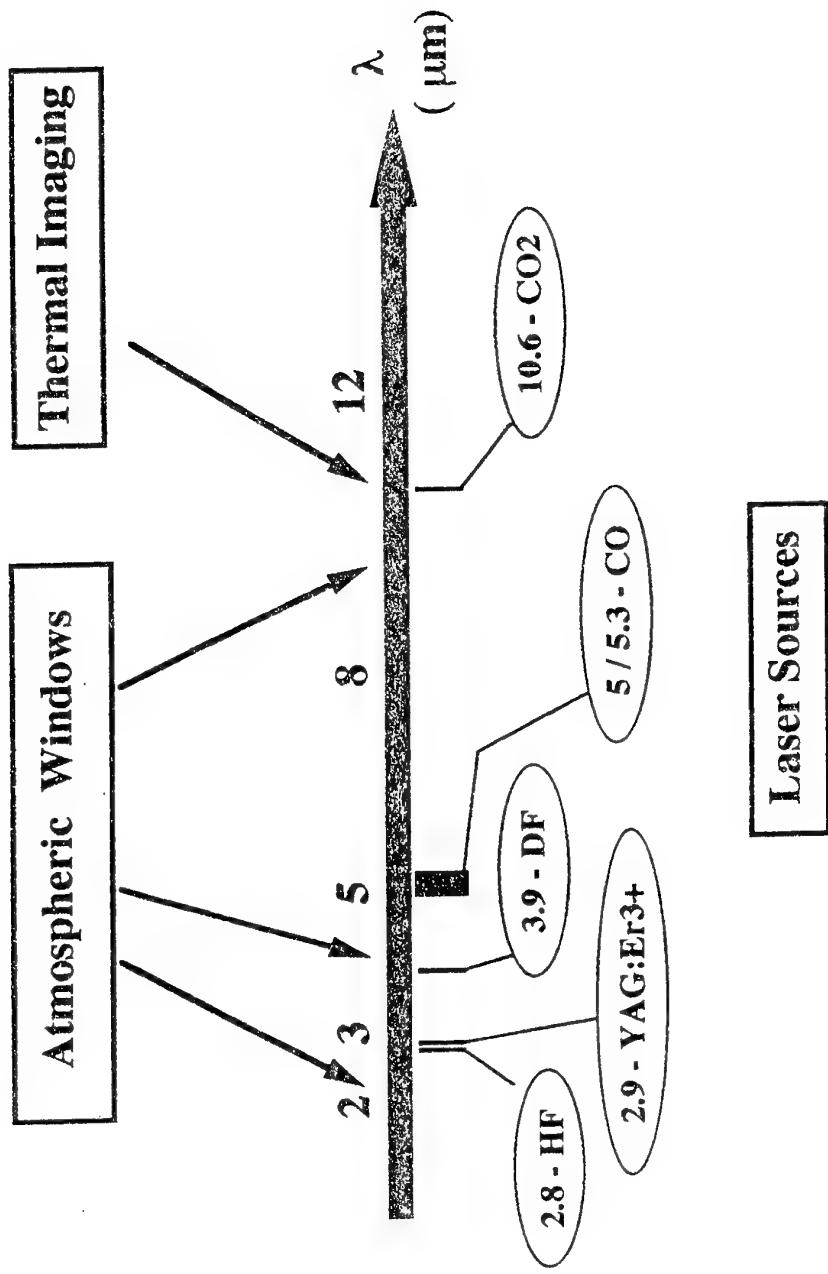
refractive index $n \geq 2.5$

Fresnel loss

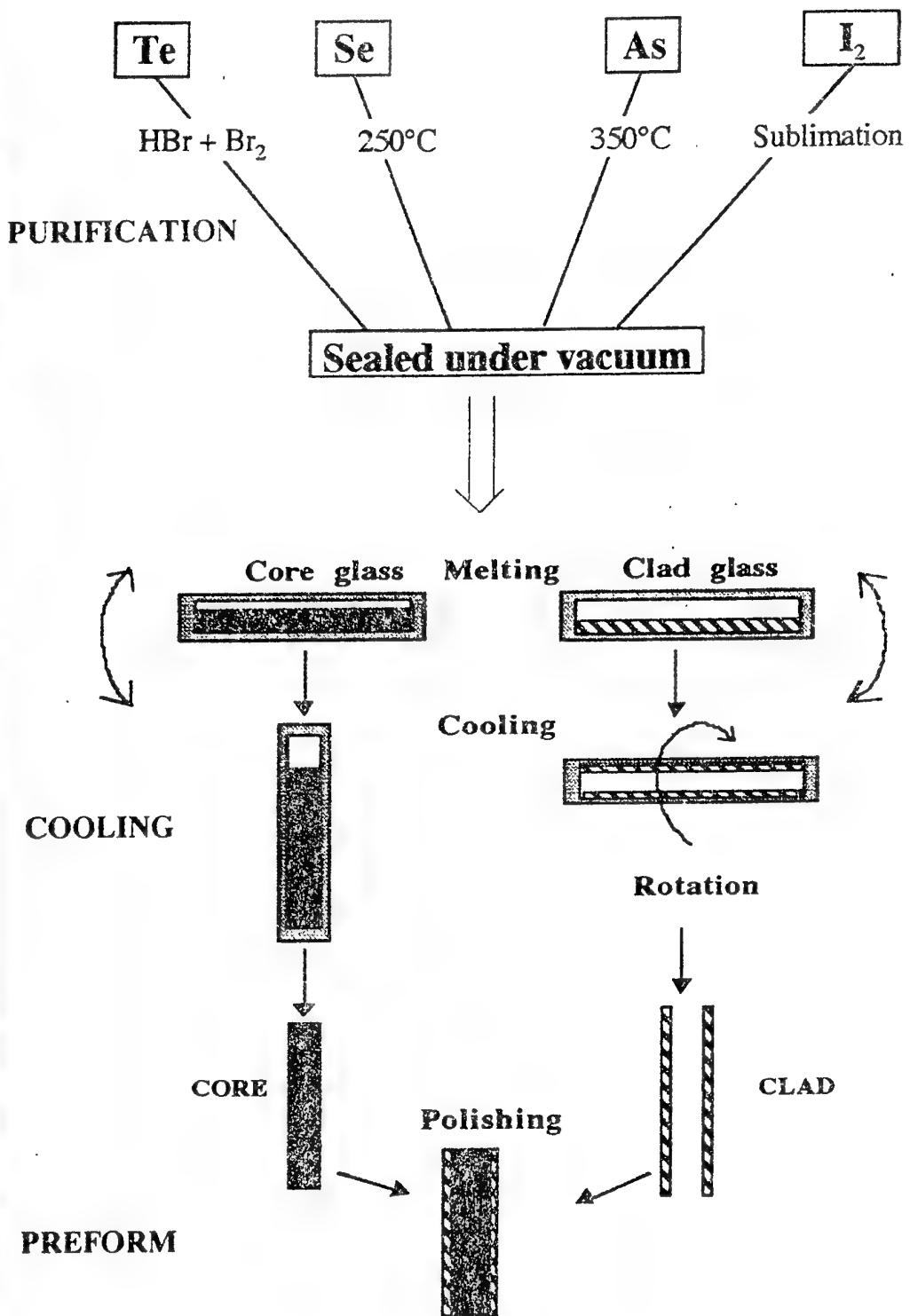


IR transmission spectrum of the $\text{Te}_2\text{Se}_3\text{As}_4\text{I}$ glass

Infrared Domains

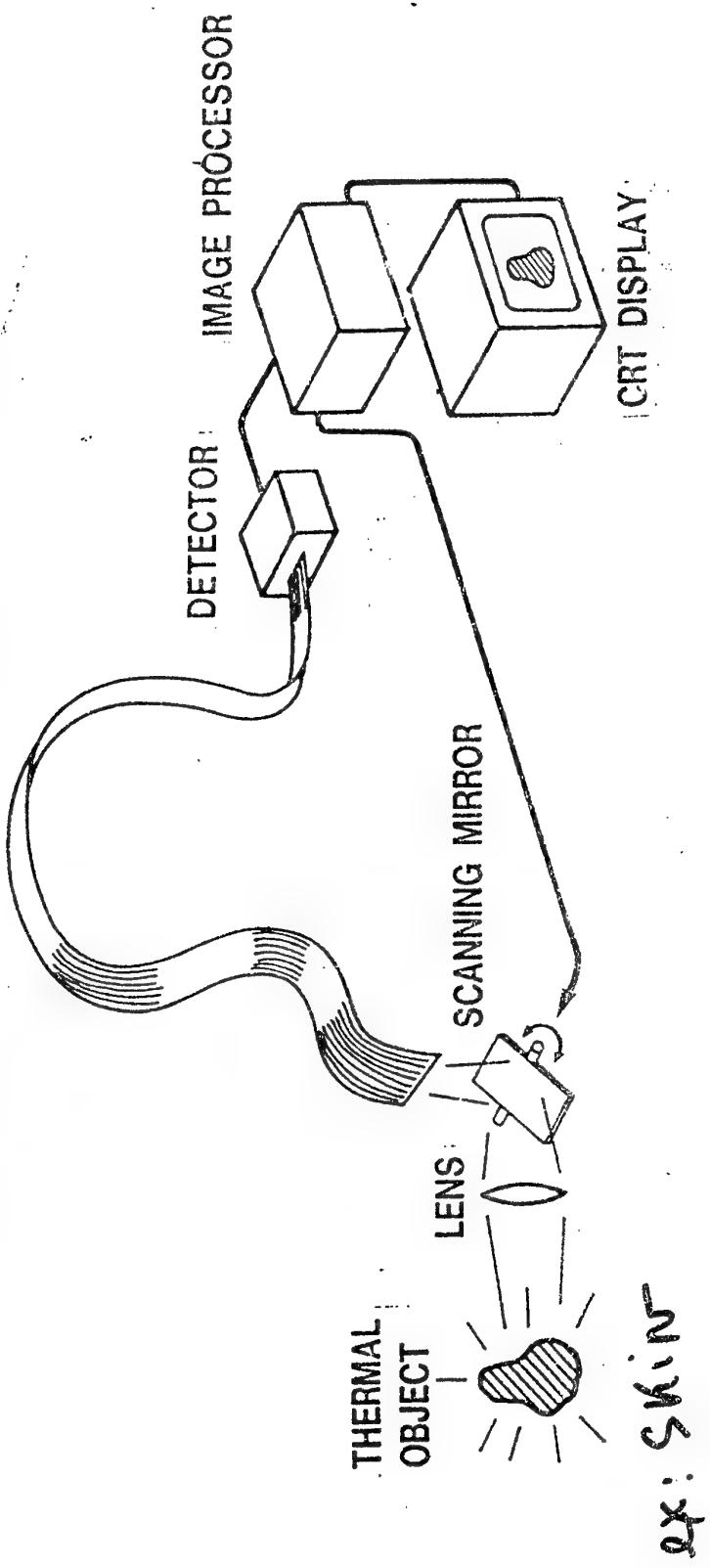


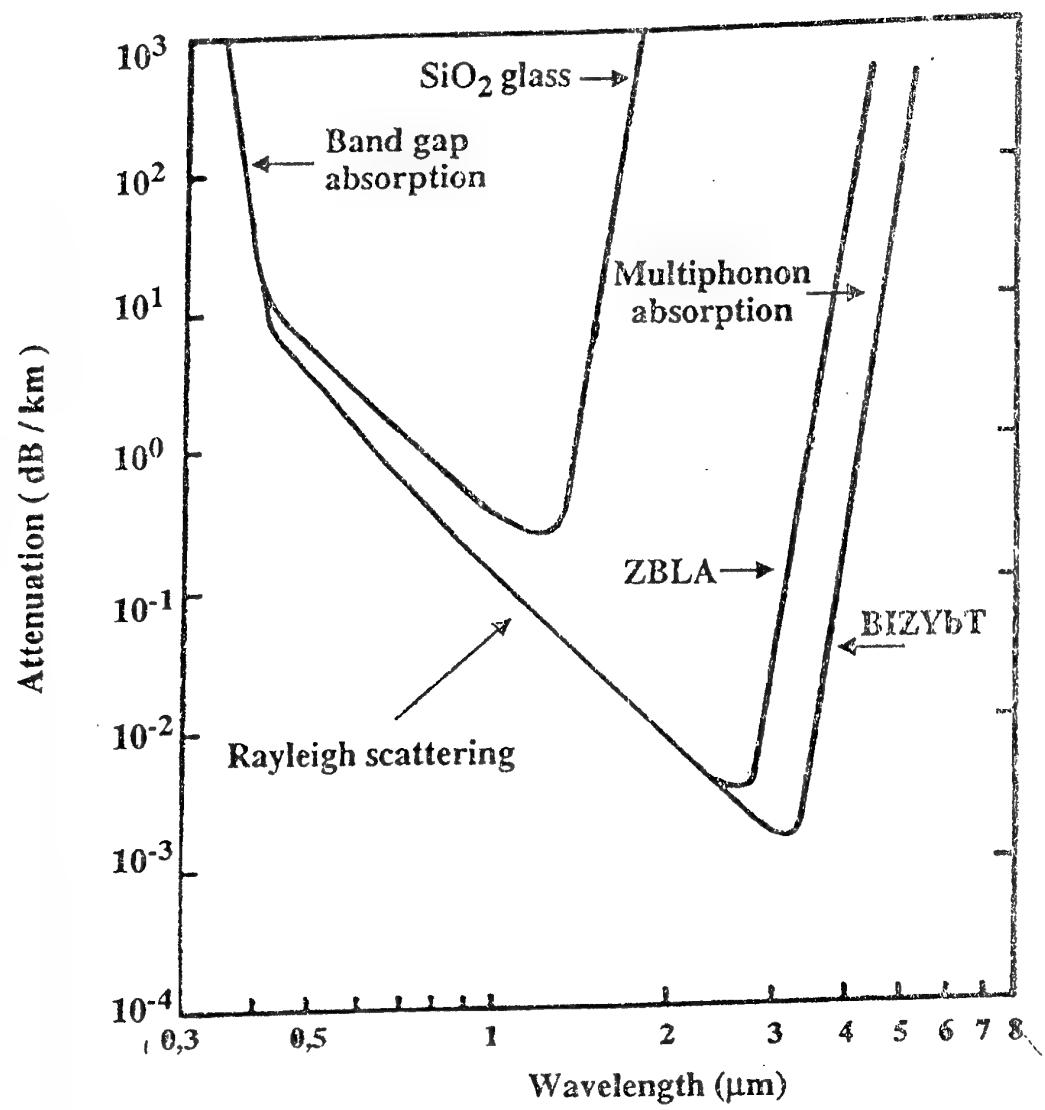
SYNTHESIS OF GLASSES

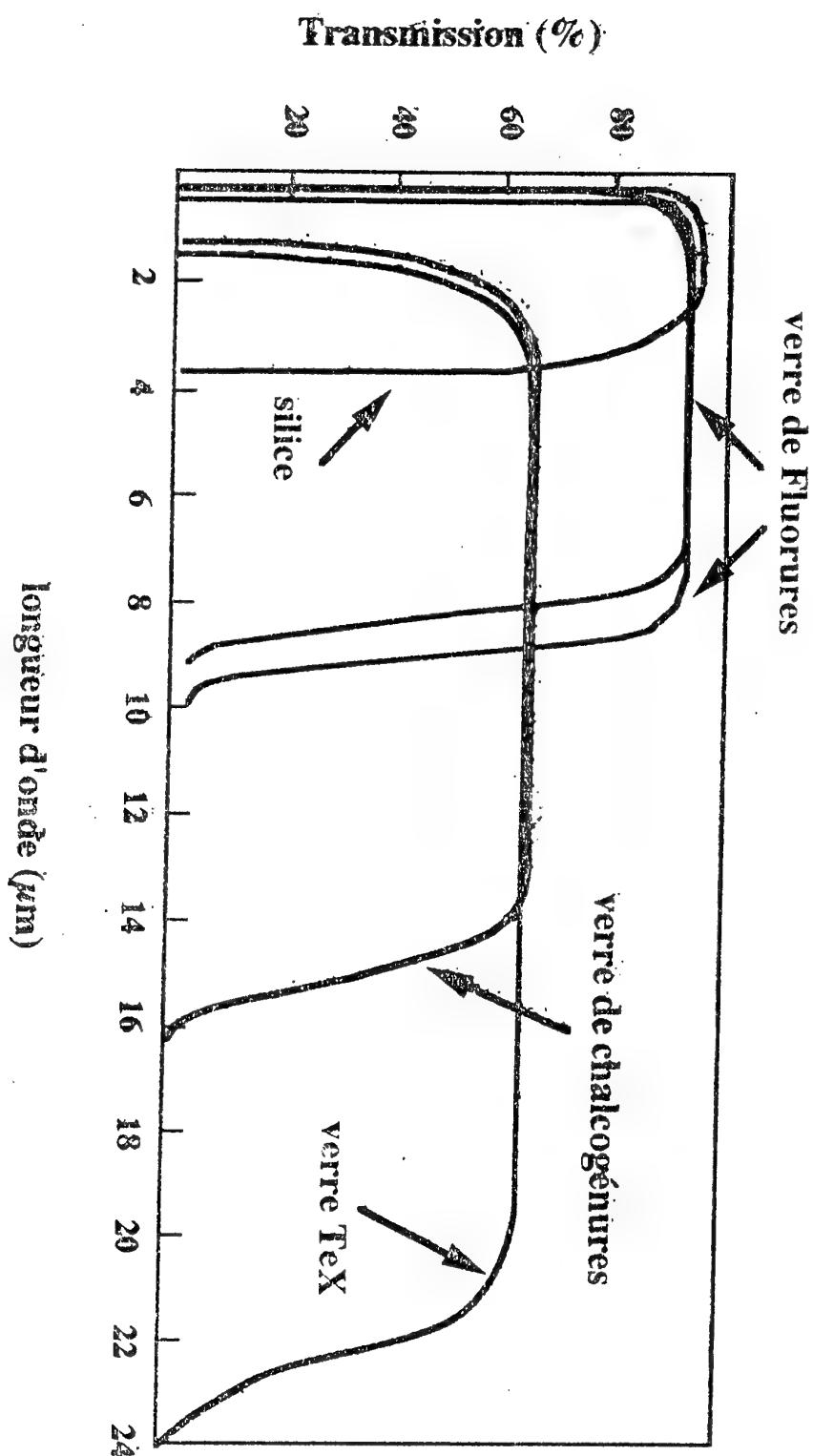


INFRARED IMAGING SYSTEM USING FLUORIDE GLASS FIBER TAPE CABLE

TAPE CABLE COMPOSED OF 80 FLUORIDE GLASS FIBERS







Comparaison de transmission infrarouge
de différents matériaux vitreux

PASSIVE FLUORIDE GLASS FIBERS

Waveguide Function

Ultra-low loss



Telecommunications
Thermal imaging

Large optical window

IR optical sensors
Energy transfer

Three FG families :

3 compositions
stable
versus
devitrification
for
Optical fiber
preparation

ZrF_4 based :

ZBLAN

→ AlF_3 based :

InF_3 based :
BIGaZYT

ZrF_4	55
BaF_2	18
LaF_3	6
AlF_3	4
NaF	17

AlF_3	25
ZrF_4	13
YF_3	11
SrF_2	45
$NaCl$	6

BaF_2	30
InF_3	18
GaF_3	12
ZnF_2	16
YbF_3	10
ThF_4	10
MnF_2	4



CANDIDATES FOR WAVEGUIDE FABRICATION

NEED

GLASS VERY RESISTANT TOWARDS MICROCRYSTAL FORMATION

DANGER : OPTICAL LOSS DUE TO SCATTERING CENTERS

GLASS RESISTANT TO MOISTURE CORROSION

DANGER : OPTICAL LOSS DUE TO OH, SH, O IMPURITIES,
PARASITIC PHONONS

→ VERY FEW N.O.GLASSES : SUITABLE FOR IR FIBERS

FLUORIDE GLASSES
MULTICOMPONENT GLASSES

ZBLAN : ZrF_4 , BaF_2 , ... based

BIG : BaF_2 , InF_3 , GaF_3 , ... based

CHALCOGENIDES BASED

As_2S_3 , As - Se - Te, ...

TELLURIUM HALIDE
TeX GLASSES

Te - Se - As - I



UNIVERSITE DE RENNES I

Laboratoire des Verres & Céramiques

Rennes - France



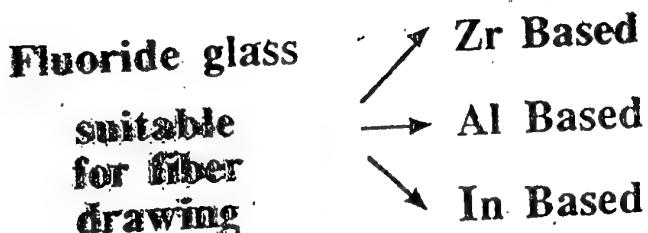
INFRARED GLASS FIBERS

1. - HALIDES BASED GLASSES

F, Cl, Br, I based glasses

→ shift of multiphonon edge

Only F based glasses stable versus moisture, corrosion and crystallisation



2. - CHALCOGENS BASED GLASSES

- As/Se, Te, S chalcogenide glasses
- Te, Se/As halogen modified TeX glasses

"Black" glasses with band gap : 0,7 → 1 eV
with multiphonon : 13 → 20 μ m.

LABORATOIRE DES VERRES ET CERAMIQUES



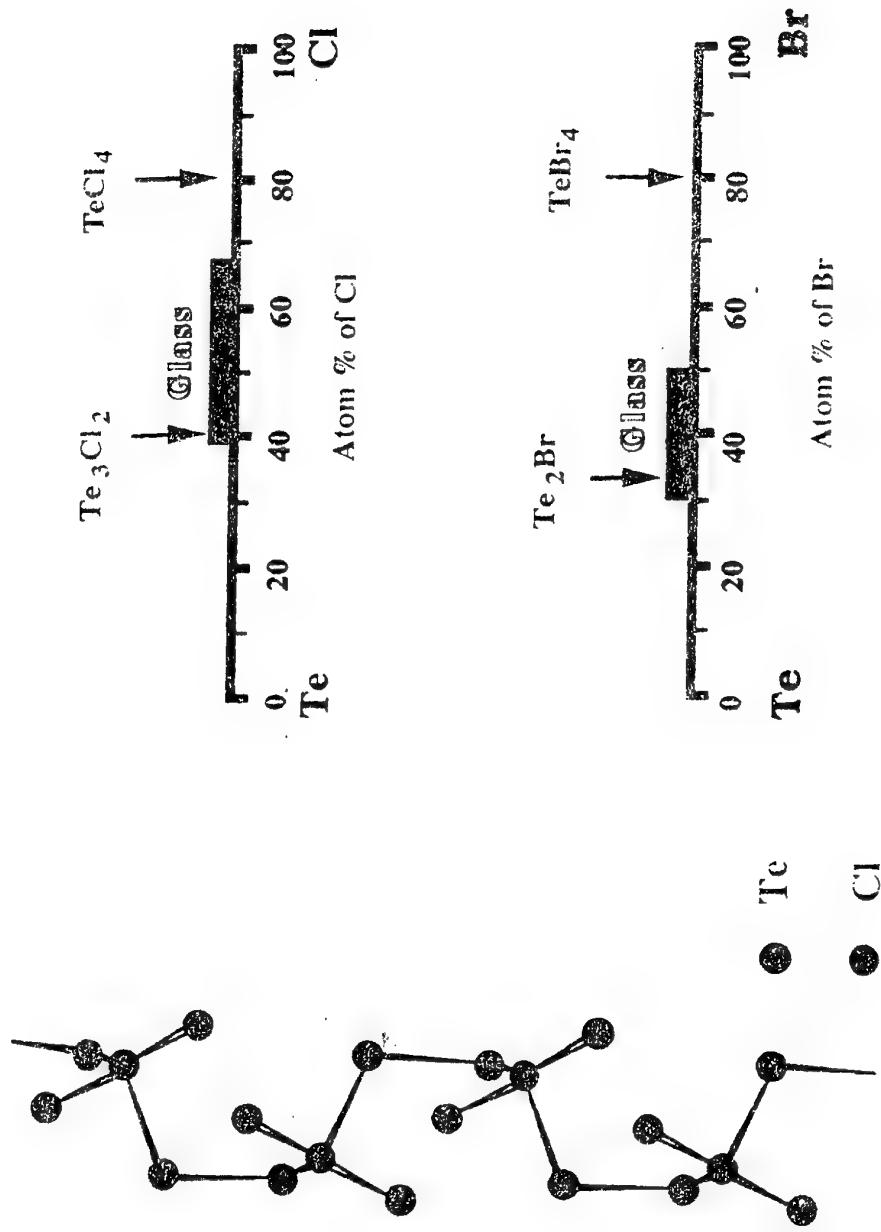
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Unité associée 1496

The tellurium halide, TeX , glasses



Crystalline structure of Te_3Cl_2

vitreous domain in Te-Cl et Te-Br systems

FUNDAMENTALS OF INDUSTRIAL GLASS MELTING

H. de Waal

1. INTRODUCTION INTO MODERN GLASS MANUFACTURING

Abstract

After a short introduction to get acquainted with the glass melting process in general, emphasis will be put on the challenges the glass-maker faces nowadays.

Keywords in this respect are: energy conservation and pollution control.

In this paper we will discuss some recent developments to demonstrate the glass technologist's struggle to respond to these new challenges. It will become clear that he often has to choose between alternative options, even without proper insight in the consequences.

To reduce flue gas emissions, for instance, the glass technologist must choose between end-of-pipe solutions and primary in-process measures. Pro's and contra's of both options will be discussed.

Among primary measures, combustion control methods to reduce NO_x , oxy-fuel firing and ways to reduce volatilisation from batch and melt are the most promising and will receive special attention.

Especially in the container industry, cullet recycling can contribute substantially in reducing flue gas emissions as well as energy consumption. Increasing the cullet content and still maintaining a high glass quality, however, is not as easy as it seems. Effects of contamination on colour, fining, foam formation and redox will be discussed.

To reduce energy consumption, the glass technologist has more options than just increasing the cullet percentage. He can install waste heat recovery systems (if he has sufficient need for low-temperature heat), but he can also improve furnace insulation (as long as that does not reduce furnace life), he can install batch and/or cullet preheating systems or he can -again- decide for oxy-fuel firing. Although this last technique is becoming quite popular lately, it is worthwhile to point out that not all the consequences of this technology on glass quality and furnace lifetime have been thoroughly investigated as yet. To be mentioned are the effect on melt and refractory of the relatively high water and alkali concentrations in the combustion room.

In addition to all these extra efforts and decisions to take, the glass technologist has to react to the demands of the customers to improve product quality, product performance and to reduce failure rates. In order to realise this, he needs better understanding of material properties, the melting process and the relation between those two.

With respect to the melting process he faces the problem that the melt is hardly accessible for accurate monitoring of chemical and physical phenomena taking place in the furnace. Partly this can be overcome by mathematical modelling. Models of the glass melting process gradually have reached the state that the glass technologist can effectively use them as a tool to optimise the process. They can describe the conditions and phenomena in parts of the furnace that are inaccessible for measurements. The validation and "fine-tuning" can take place by comparing mathematical results with those of measurements of phenomena that can be measured experimentally.

2. BATCH MELTING

Abstract

Most glass batches are a complex mixture of components, some of which are highly reactive and melt easily, others are more inert and melt only at very high temperatures.

An overview will be given of the chemical and physical phenomena that take place when this mixture is heated in the glass furnace.

Special emphasis will be placed on the kinetics of the batch melting process, since that determines the maximum output that can be realised.

After melting down of the batch, the liquid is still full of unmolten particles, sand mostly. The dissolution rate of these grains depends on the diffusion constants, the solubility and on the convection flows in the furnace. The effects of these parameters will be discussed in detail.

Also, it will be shown how this process can be optimised with the help of mathematical models that exist nowadays of the melting process, including heat and mass flow distribution and particle tracing techniques.

3. THE FINING PROCESS

Abstract

Fining is one of the sub-processes, taking place in the furnace, in which the gas bubbles are removed from the melt. It is usually enhanced by small additions of sulphates or antimony oxide.

It will be explained how these so-called fining agents function and under what conditions in the furnace their functionality can be optimised.

It will be shown that the redox of the melt is of the utmost importance for this process. The influence of diffusion constants and solubility of the gases on bubble growth and shrinkage will be explained. Bubble shrinkage and resorption takes place during the secondary fining process, which is predominant in the last part of the melting furnace, where the glass cools down from 1500 till about 1200 degrees C.

Finally the phenomenon of reboil will be discussed and the possibilities to optimise the fining process with mathematical models, making use of bubble tracing techniques.

4. VOLATILISATION AND DUST FORMATION IN GLASS FURNACES

Abstract

Volatilisation is the primary source of emissions from glass furnaces. Also, it reduces glass quality, since it gives rise to inhomogeneities.

The numerous sources of volatilisation will be discussed and it will be shown how the process can be minimised. The effect of glass composition is predominant for this process, so that will receive special attention.

The recently introduced oxy-fuel combustion technique, making use of oxygen instead of combustion air, strongly influences volatilisation of certain components, so it will be discussed separately.

Results of laboratory experiments will be compared with observations during industrial glass melting and finally the results of modelling studies will be presented.

5. FOAM FORMATION DURING GLASS MELTING

Abstract

During the industrial glass production a foam layer is undesirable since it acts as a thermal insulator, reducing the heat transfer from the burner flames to the molten glass

bath. The reduced heat transfer leads to a higher energy consumption and an increased wear of the crown as a result of higher temperatures in the combustion chamber. Nowadays, renewed attention is paid to the foaming problem as a result of increasing energy prices in combination with both new process operations and technologies promoting foaming.

From industrial observations it is known that foaming becomes more critical in furnaces using cullet with high levels of organic contaminants and sometimes foaming becomes more intense after changing to oxy-fuel firing.

From samples scooped from industrial furnaces producing sulphate refined soda-lime glass contain, apart from some CO and CO₂, large quantities of SO₂-gas, indicating that the sulphate chemistry plays an important role during foaming.

In this lecture the nature of the different kinds of foam in glass furnaces will be explained and the effect of parameters such as temperature, batch composition, redox of cullet mixtures and the furnace atmosphere on foaming and foam stability will be discussed. Ways to avoid or at least decrease foaming will be indicated.

For fluor, the dependence of fluor emissions on the fluorine carrier is clearly shown in figure 4, where fluor balances are shown for a flint glass and a green glass furnace. In the flint glass furnace, the fluor emission is about 6% of the total fluor input, whereas in the green glass furnace, with a cullet level as high as 90%, the fluor emission level amounts to 11% of the total input. Obviously, cullet "loses" more of its fluor than other fluor carriers.

3. Energy Conservation Technologies

During the last decade batch/cullet preheat technologies [7,8], oxy-fuel firing [9], the increase of cullet usage, combustion modifications, improvements in regenerator efficiency and better insulation of the furnaces have led to remarkable energy savings.

Further optimisation of batch/cullet preheating systems will certainly lead to a wider application of this technique, particularly in cases, where boosting plays a role to increase furnace load and in combination with oxy-fuel firing, since in this case savings in oxygen add up to the savings in fuel.

Oxy-fuel glass melting technology is one the most important developments in glass technology today, especially as an alternative for recuperative furnaces. Replacement of a recuperative furnace by an all oxy-fuel fired melter will reduce the specific primary energy consumption by 25-35 %.

Oxy-fuel firing may create unexpected and partly unexplained effects, though. The combustion chamber of an oxy-fuel fired furnace contains relatively high water concentrations (50-60%, compared to 12-18% for air-gas fired furnaces) and because of the very low gas volumes, the concentration of volatilisation products is high in the combustion chamber.

It has been found that the melt in an oxy-fuel furnace contains significantly more water than in a gas-air fired furnace under identical conditions. Whether this is caused by increased penetration from the combustion chamber or by suppression of vaporisation of batch water is not clear yet. The water, however, appears to partly replace the oxidising sulphate groups in the melt. This affects the redox conditions and therefore properties that depend on redox, like colour stability, fining and foam behaviour. To illustrate this point, fig. 5 compares the oxygen activity in amber container glasses molten in oxy-fuel and in gas/air fired conditions.

The impact of the high water concentrations on glass melting chemistry and on the glass melt properties and the consequences of the high alkali concentration in the combustion space on -for instance- refractory corrosion during the furnace life are not well understood as yet.

Challenges for the future include the realisation of new furnace designs that combine energy conservation with low emissions and high product quality. At the moment several approaches have been made and described in the literature [10]. Perhaps a bit speculative it could be concluded that two developments seem to be the most promising, especially when combined:

- better separation between the melting and fining process, going into the direction of plug flow, to increase the minimum residence time and to reduce the width of the residence time distribution.
- better heat transfer of the flue gases to the batch in the furnace by directing the

flue gases in counter flow over the batch before leaving the furnace. This is an especially useful approach for oxy-fuel fired furnaces.

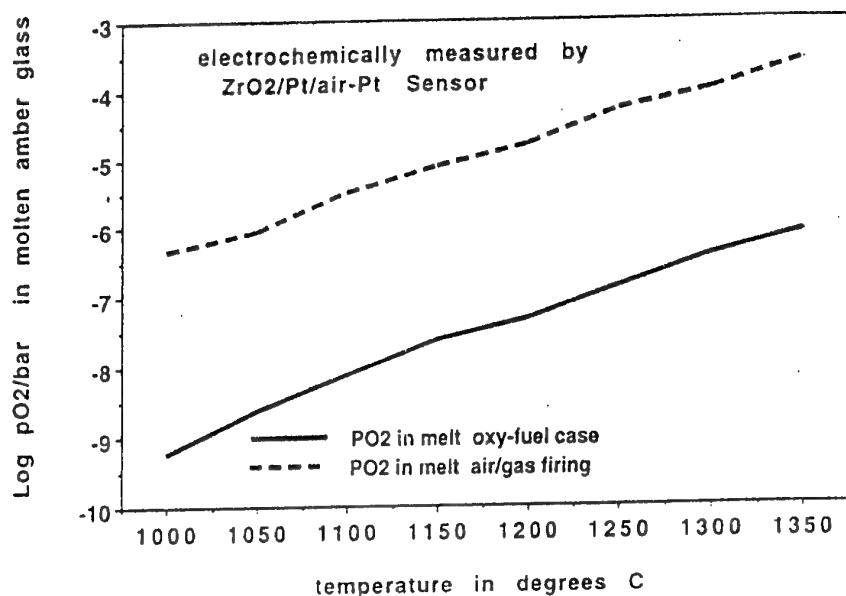


Fig. 5 Oxygen activity in an amber container glass melt under different furnace conditions

4. Recycling

Cullet recycling has an effect on flue gas emission as well as energy conservation [11,12]. Reason enough to discuss it separately and in more detail here.

Recycled cullet has become the most important raw material for the green and amber container glass manufacturer. In Western Europe about 50% of the container production is recycled. In some countries this percentage is as high as 30%. Today, cullet levels of 80% are not unusual for green and amber glass. It can easily be predicted that this percentage will go up in the near decade. Cullet significantly reduces energy consumption, for melting as well as for the production of raw materials (soda!) and also reduces the emission of particulates and SO₂.

There are, however, some technological problems to be solved, mainly because the cullet is not very constant in quality. The glass producer has continuously to correct the cullet rich batch composition in order to obtain products with the required colour and with an acceptable seed count.

Contaminants like fragments of ceramics, ferro- and non ferro metals, non soda lime glasses and organic materials generally affect the product quality or have undesired effects on the melting process like: foam formation, increased volatilisation (lead, fluor, as shown in fig. 4) or incomplete fining. Another important point is the variety in glass colours in the mixed cullet.

The purification of cullet and ways to characterise the cullet (contents of organic materials, quantities of different colours) in order to make the right corrections for obtaining the required redox state and colour of the glass are very important issues in the container glass industry today. Investigations on redox behaviour during the

melting of glass and the chemistry of sulphates in the melt are necessary to find the relations between the batch composition, glass melting process (temperatures), furnace atmosphere on one hand and the redox state, the fining efficiency and the glass colour on the other hand.

The complexity of this problem is illustrated by the fact that the oxygen activity of a melt produced from (mixed) cullet even depends on the "age" of the cullet. A few months cullet storage may very well raise the oxygen activity of the melt, by two orders of magnitude because of fermentation of organic material in the cullet [13]. Without rapid and reliable methods to characterise the redox state of the cullet mixtures, including organic contamination, the glass manufacturer will not be able to increase cullet percentages further without serious problems with quality. These methods, however, have still to be developed.

5. Glass Quality

The improvement of the glass quality has always been one of the major concerns of the glass producer. The competition of the different materials in the packaging sector is the driving force to make container glass even more reliable and to develop high quality lightweight products. For other products it may be the customer who sets the standard, mainly by comparison. In all cases it is clear that rejects affect price and energy consumption.

Optimisation, control and better understanding of the melting and forming processes have been recognised by the glass industry to be of key importance in improving quality and reducing reject numbers.

Nowadays, mathematical modelling has become a standard tool for major producers of float glass, T.V. glass and fiberglass. Also for container glass furnaces, glass tank modelling proves to be a valuable method to optimise process conditions.

Mathematical modelling is no longer just a way to visualise the flow patterns and provide data on heat transfer. It can also predict glass quality in relation to process parameters, because all chemical and physical phenomena are included in the latest generation of models, based on experimental and theoretical research of these phenomena [14].

Sub-models have been developed to investigate, by mathematical modelling, the effect of bubbling, electrical boosting, initial sand grain size, pull rate etc. on the melting behaviour. Obviously, all these sub-models are linked to the basic glass tank model. Three dimensional glass tank modelling in conjunction with sub-models describing melting kinetics or behaviour of gases and gas bubbles in a melt appears to be an important tool for the optimisation of furnace design and the melting process and can even be used to investigate new furnace designs. Figure 6 gives an example of such a study, where an attempt is made to separate the melting and fining processes.

Further extensions of these models will fulfil the need to obtain complete understanding of the influence of adjustable process parameters (like pull rate, bubbling, boosting, firing) on the presence of stones, knots and bubbles in the product, and also on homogeneity and colour.

Further developments will be directed towards modelling of time-transient behaviour and integration of models into furnace control procedures. Back tracing

techniques for cords, seeds and stones will be combined with statistical methods to improve existing procedures for defect-source diagnosis.

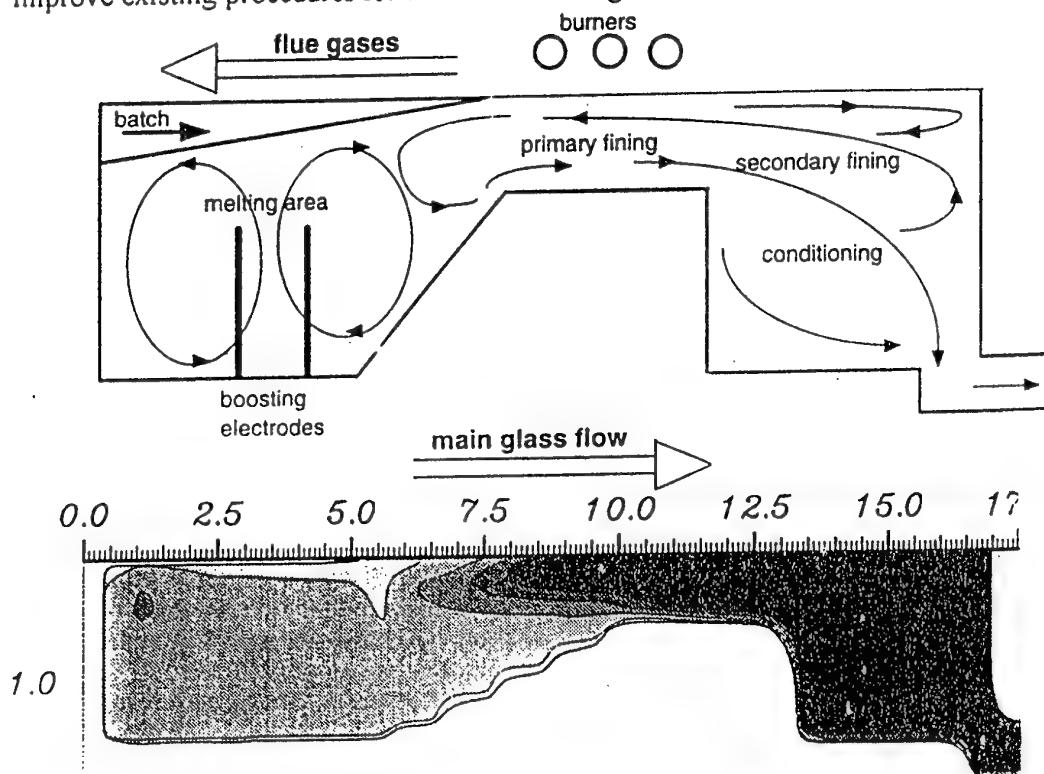


Fig. 6 Simulated melting tank with attempt to separate subprocesses. (Dark area represents high temperature, in steps of 40 °C down from 1510 °C).

By using back tracing techniques, the origin of glass defects, like bubbles with a certain size and composition, or the source of unmolten material found in products, may be discovered. This could become an important tool for furnace operators and trouble-shooters to identify the causes for process calamities and to localise defect sources.

Glass tank modelling in combination with glass quality sub-modelling is still in a stage of development. Further validation of the obtained results and accurate determination of relevant molten glass properties like radiation transport and the behaviour of gases in glass, are essential to increase reliability and applicability. The combination of glass tank modelling with furnace control concepts and glass defect analysis are future challenges for R&D in glass technology.

6. Concluding Remarks

Glass manufacturing, although one of the oldest technologies in the world, is not a static process. Changes occur from inside the glass world by our desire to improve the material and its products and also due to forces from outside, mainly to protect our environment. For a proper response, the consequences of modifications in the glass production process should be understood and anticipated.

BATCH MELTING KINETICS

A. Reactions in batch blanket

Fast melting components:

soda, limestone, sulphate, dolomite → primary melt

Slow melting components, dissolving into the primary melt:

sand, nepheline, feldspar

At 1200 °C 60 % of the sand dissolves within 30 minutes into the primary melt of the batch blanket

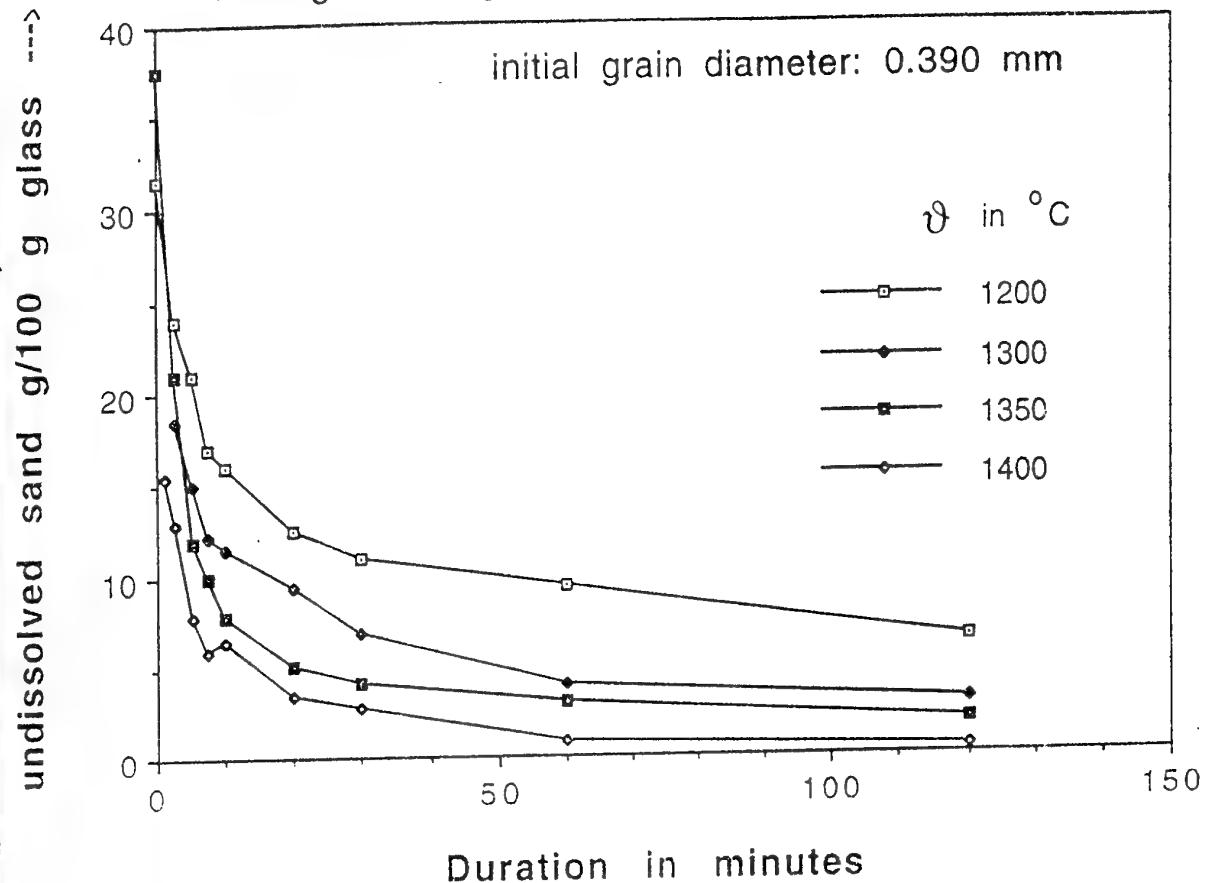
B. (Partly) undissolved grains go into the glass melt and dissolve later.

This process is governed by:

- diffusion rate of SiO_2 in the melt (depends on temperature)
- solubility of SiO_2 in the melt (depends on temperature)
- convection currents in the melt

Alumina dissolves 10-50 times slower into the glass melt than sand grains!

Effect of temperature on melting and dissolution of sand grains in glass melt and batch



HOW TO INFLUENCE THE FLOW PATTERN?

- Temperature profile in combustion room (crown temperatures) → hot spot
- Electrodes in melt (boosting)
- bubbling
- batch feeding, position and shape of batch blanket
- tank design (length/width/depth of glass bath)
- dams, raised or lowered parts of furnace bottom
- cooling of side walls (results in flow in width direction)

To be optimised with mathematical modelling of the furnace.

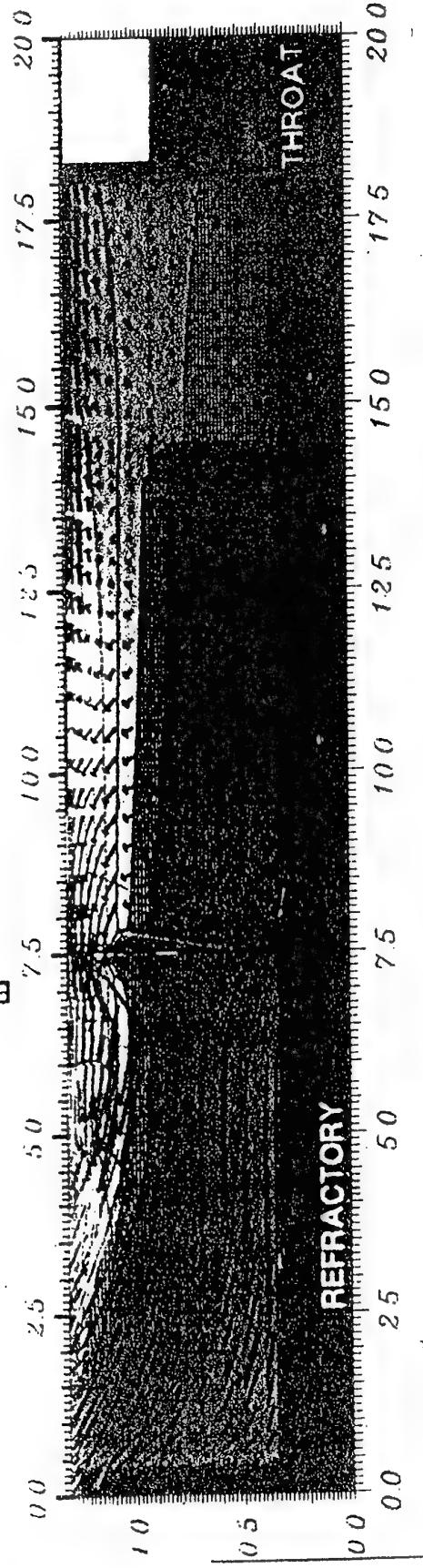
Velocity distribution in the pipe at the

bottom of the pipe with bubble building [°C]

Velocity [mm/s]

—	14.0	12.2
—	9.79	11.0
—	8.57	9.79
—	7.35	8.57
—	6.12	7.33
—	4.30	6.12
—	3.67	4.80
—	2.45	3.67
—	1.22	2.45
—	0.00	1.22

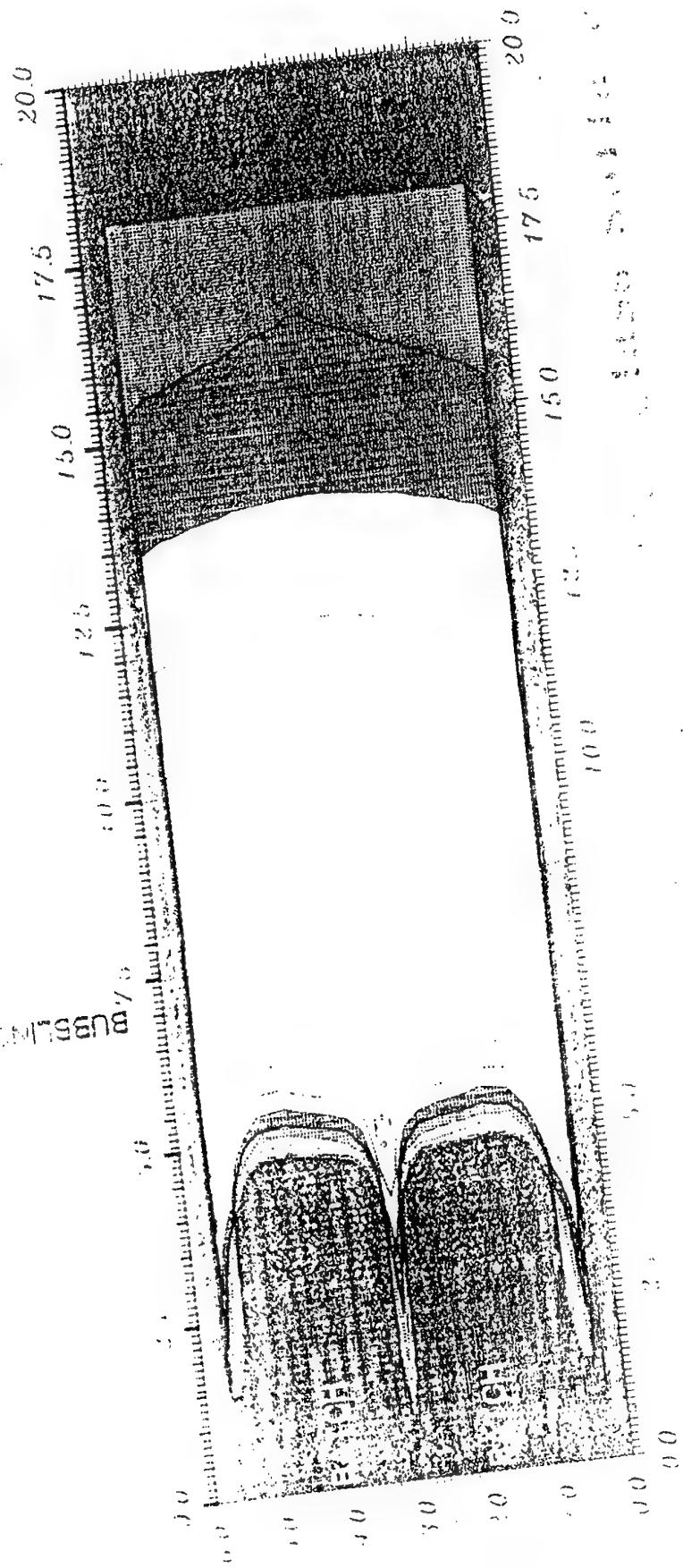
BUBBLING POSITION



Refractive index : 1.2242 E 02
 Throat height : 1.1631 E 02
 Scale length : 1. Y : 5 Giga-Ohm of 1000
 Refractive index : 1.0000000000000002

CO₂ 1500

1500.
1475.
1450.
1425.
1400.
1375.
1350.
1325.
1300.
1275.
Below.



EFFECT OF REDOX ON FINING

High redox:

- high oxygen pressure in the melt
- high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio
- high sulphate retention
- high fining temperature needed

low redox:

- low oxygen pressure
- much Fe^{2+}
- low sulphate retention
- low fining temperature needed

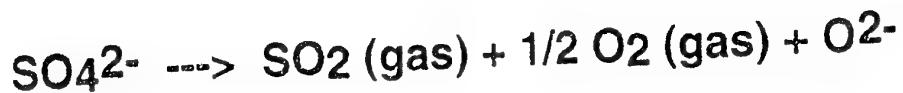
very low redox:

- gives amber glass, due to $\text{Fe}^{3+}-\text{S}^{2-}$ complex formation

ROLE OF SULPHATE

- o oxidiser for melt \rightarrow higher redox
- o addition of organic material, sulphide or cokes lowers the temperature where the fining gases O_2 and SO_2 are formed in large quantities.

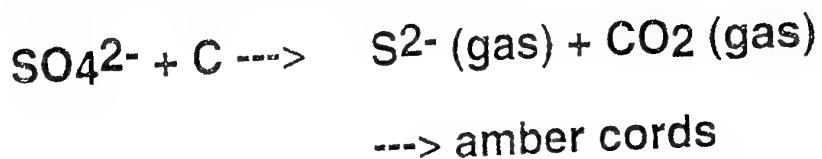
In oxidized melts (often > 1350-1400 °C):



Slightly reducing melts (at lower temperatures):



Very reducing conditions:



- o Sulfate solubility increases at increasing pO₂
- o Sulphide solubility decrease at increasing pO₂

Refining or secondary fining:

Only when primary fining is efficient enough !!!

Efficient primary fining:

- o only small quantities of dissolved gases remain in the melt
- o bubbles > 1 mm have been removed

Bubbles with gases showing a increasing solubility in the melt after lowering temperature can now be resorbed:

Example: SO₂, O₂ or CO₂ bubbles

Nitrogen dissolves only very slowly.

Fining process in melting tanks:

Models:

- a. Calculation of release of gases in melt by fining/redox reactions ---> redox model

result: vapor pressures and gas concentrations in melt at every position

- b. Tracing of trajectory of single bubbles

- c. Bubble changes by "bubble behaviour model":

- diffusion of gases into/from bubble depending on:
 - o bubble size
 - o bubble composition
 - o local gas concentrations
 - o temperature
 - o convection
- bubble growth or shrinkage
- ascension velocity

---> change in bubble size, bubble position
bubble composition

Typical defects incomplete refining

- S1. CO₂ and N₂ containing seeds
(Ar in seeds ---> air inclusions)
- S2. large bubbles containing: SO₂ and gases diffusing in growing bubble: N₂, CO₂ or Smokey blisters*
- S3. CO₂-bubble 0.4 - 1 mm
- S4. SO₂ containing bubbles (plus N₂)
relatively large: > 0.5 mm
very reducing conditions: COS, H₂S, S₂ or Smokey blisters*
pure N₂ bubbles without Ar
- S5. CO₂/N₂ bubble
- S6. Larger bubbles > 1 mm with:

10-15 %	CO ₂
0-3 %	O ₂
10-20 %	H ₂ O
60-70 %	N ₂
0.8 %	Ar
- S7. Original O₂-Bubbles may change into bubbles:
20-50 % N₂
5 - 30 % CO₂
about 50 % SO₂
no Ar

Critical conditions:

1. **Short cut glass current in melting tank**
 T never reaches T_f or only during very short time ---> incomplete primary fining
2. **High temperatures in throat and rapid cooling in forehearts and feeders ---> resorption time insufficient (1350-1200 °C)**
3. **Mixing of glass melt from bottom and surface in throat ---> reboil !!!**
4. **Nitrogen bubbles < 1 mm**

Volatileisation in Glass Furnaces

1. Introduction

The origin of the emissions of glass furnaces and the process conditions which determine the emission levels for particulates, boron, lead, chlorides and fluorides are investigated using literature information, modelling studies and measurements in the glass industry.

The origin of flue gas emissions in glass furnaces can be:

- o the combustion process which is often the major cause of the NO and NO₂ emissions;
- o the batch blanket which releases volatile components like selenium compounds (SeO₂), HF, HCl and at reducing conditions also SO₂.
- o carry-over of fine particles from the batch blanket;
- o volatilisation from the glass melt surface, like the release of NaOH, NaCl, PbO, NaBO₂, KBO₂, HBO₂, SO₂, As₂O₃ and Sb₂O₃ vapors.

NaOH and HBO₂ are products from a reaction of water vapor in the furnace atmosphere and oxides in the melt (Na₂O and B₂O₃).

Most important emissions from fossil fuel glass furnaces are NO_x components produced in the flames or originating from nitrate raw materials.

Other emissions in different glass production processes:

Soda-lime-silica glass furnaces:

- o Sodium sulphates particulates, the major component in flue gas dust;
- o Lead oxide mainly as particulates in furnaces using external recycling cullet;
- o Glass batch dust from carry over;
- o HCl gas;
- o HF gas;
- o SO₂ and SO₃ gas;
- o SeO₂ gas in flint glass furnaces.

Below 250-300 °C the sodium sulphates will be converted into sticky and corrosive NaHSO₄ or Na₂S₂O₇ in SO₃ rich flue gases.

Lead glass (T.V. glass tubes, crystal ware):

- o Lead oxide and lead sulfate (in oil fired furnaces);
- o Potassium carbonate dust;
- o Arsenic oxides, which are partly gaseous > 100 °C;
- o NaCl and KCl particulates;
- o HCl gas.

Borosilicate glass furnaces (insulation wool, E-fiberglass):

- o Particulates containing sodium meta- and tetraborates (NaBO₂ and Na₂B₄O₇);
- o Particulates containing potassium borates (E-glass);
- o H₃BO₃, sublimating at 130-150 °C in flue gases of E-glass furnaces;
- o Particulates containing sodium and potassium sulfates;
- o HF gas in E-glass furnaces;
- o HCl gas;
- o SiO₂ particulates, originating from carry-over of fine quartz powder or from SiF₄ volatilisation;
- o SO₂ and SO₃ from sulphate fining.

The emission levels of the above mentioned components depend on:

- input of the different chemical components (Cl, F, Na, B, S, K, Pb etc.) in the furnace;
- the kind of raw materials which carry these components;
- the kind of contaminants in the raw materials;
- the temperature at the surface of the glass melt;
- the composition of the glass;
- the composition of the furnace atmosphere;
- the flue gas velocity above the batch blanket and the glass melt;
- the humidity of the batch.

In most cases the volatilisation processes from the batch blanket and the glass melt determine the emissions of particulates, HCl, HF, selenium compounds, lead compounds and boron compounds.

Today, volatilisation models can be applied to find the relations between process conditions and expected emission levels.

Partly reduction of emissions of all the mentioned components can be achieved by primary measures like the choice of alternative raw materials, modifications in the process conditions, changes in the applied fuels or changes in the furnace designs.

2 Sources of particulate emissions

In soda-lime glass furnaces three main sources for the emissions of particulates can be distinguished:

1. Metal impurities in the fuel: fuel oils contain small concentrations of vanadium, sodium and nickel components. The maximum particulate formation levels from these sources are about 5-10 mg/sm_n³.
(1 sm_n³ = standardized to conditions: 0 °C, 1 bar, dry gas and 8 % oxygen)
2. Batch carry-over, the raw materials containing fractions with particle sizes below 20 micrometer can be sensitive to some carryover. Sampling studies [1-5] and the chemical analysis of almost sub-micron sized [6,7], only sulfur and sodium rich dusts from soda-lime glass furnaces leads to the conclusion that carry-over in these modern furnaces contribute to not more than 5 till 15 % of the total particulate emissions.
3. Volatilisation: different vaporisation processes can be distinguished:
 - a. Volatilisation of pure components from the surface of the batch blanket, like sand, feldspars, lime and soda. Vapor pressures of these components are very low at temperatures up to 1200 °C. Above 1000 °C the single components already have been reacted to form silicates and therefore, the vapor pressures of batch components above the reacting batch blankets, will be relatively low;
 - b. Reactive volatilisation by chemical reactions at the batch blanket surface with components in the furnace atmosphere. Thermodynamics and literature data [8-13] show that the water vapor in the combustion chamber may be important for the reaction of soda to form sodium hydroxide vapors:



Similar reactions (formation of KOH) take place for potassium carbonates.

Figure 1 shows the influence of the temperature at the surface of the batch blanket on the equilibrium vapor pressure of NaOH, in a furnace atmosphere with 20 (in the case of gas/air firing) and 60 vol.-% water (the oxy-fuel fired case).

The reactive volatilisation process will be important at parts of the batch blankets, which have surface temperatures high enough: > 900 °C, to obtain sodium hydroxide vapor pressures above 10 Pascal, but also having temperatures lower than the formation temperatures of sodium silicates or sodium-calcium silicates. Above 900-1000 °C, the main part of the soda probably will have reacted with the other raw materials. Then the chemical activity of the sodium components in these melts will drop, leading to very moderate NaOH vapor pressures.

- c. Volatilisation of sodium compounds in gas bubbles during the fining process. A balance on the bubble evolution from glass melts shows the minor importance of this source in the total release of sodium components from the melt.
- d. Volatilisation of NaCl as an impurity in synthetic soda. This salt has a relatively high vapor pressure above 800 °C and leads to some NaCl vapors at higher temperatures. Nowadays chloride concentrations in the batch components have been reduced considerably and NaCl volatilisation hardly contributes to the total sodium volatilisation in the furnace. Less than 10 % of the sodium may come from this volatilisation process.

NaCl volatilisation from the batch:



In cooling SO₂ containing flue gases below 1100 °C :



- e. Thus, this process gives extra particulates (Na₂SO₄) as well as HCl (gas) emissions.
- f. Volatilisation of sodium sulfate from the surface of the molten glass. Although the vapor pressures of Na₂SO₄ are rather low, volatilisation may take place because the chemical activity coefficient for sodium sulfate in molten glass can be relatively high.
- g. Reactive volatilisation from the glass surface. The sodium oxide in the silicate melt reacts at the surface with water vapor:



Although, the activity coefficients [14,15] of sodium oxides in molten silicates are very low: 10⁻⁶ - 10⁻⁷, this reaction will be important above 1200-1300 °C. The vapor equilibrium pressures of sodium sulfate, sodium or sodium oxides are at least one order of magnitude lower than sodium hydroxide pressures in water vapor containing furnace atmospheres. In figure 1, the influence of glass surface temperature and water vapor pressure in the atmosphere has been given for sodium hydroxide vapor pressures in equilibrium with a soda-lime glass melt with 12 weight-% Na₂O (attention, the scaling of the vapor pressures is logarithmic). At reducing conditions, sodium (as Na) vaporisation by reduction of Na₂O might take place. The volatilisation of NaOH by reaction 2.4 is probably the major source of particulate emissions in soda lime glass furnaces.

Sodium sulfate at the glass melt surface might volatilise forming sodium sulfate vapors. But these vapors are thermodynamically very unstable above 1300 °C. More likely is the reaction:



- g. This reaction might become important at SO₃ concentrations in the melt > 0.2 wt-%. In case of recycling of external waste glass, emissions of lead components (PbO, PbCO₃ or PbSO₄) might take place because of lead glass and metallic lead contaminants in the applied external cullet. Especially, the lead glass will cause emissions of lead components up to 15 mg/sm₃, due to PbO volatilisation from the melt. At local reducing conditions pure lead may vaporize directly from the melt, for instance for amber glass melting. Reducing conditions, for instance in locally reducing atmospheres, promote the lead volatilisation and particulate lead emissions.

3. Observations during industrial soda-lime glass melting

Soda-lime glass furnaces

From dust analysis data for float and container glass furnaces, we may indeed conclude that sodium is the major component leading to dust formation in flue gases (by condensation) from soda-lime glass furnaces.

In very sulfur lean flue gases, sodium chloride, sodium fluoride or sodium carbonate particles can be formed during the cooling of the flue gases below 900 °C. But these situations are rare, sometimes, for instance in the case of antimony, instead of sulfate refined melts and using natural gas firing, these non-sulfate components are more important in the composition of the particulates.

For most of the soda-lime glasses, sodium sulfate as a fining agent is used. The dissociation of this sodium sulfate in the molten glass leads to sulfur oxide concentrations, which are much higher than the sodium component concentrations in the combustion chamber and in the flue gases. During the cooling process of the flue gases, the sulfur oxides react with almost all the sodium components, mainly sodium hydroxide [16], obtaining sodium sulfate in condensation below 1100 °C. This leads to the well known deposition of sodium sulfate in regenerators, recuperators or heat exchangers or formation of submicron droplets. Below 884 °C these droplets crystallize and generate sodium sulfate particulates. Figure 2 shows schematically the volatilisation mechanism and the condensation reactions. Typically flue gas dust from soda-lime glass furnaces contains particulates in the range of 0.02 till 0.5 micrometer [6]. X-ray diffraction proofs that Na₂SO₄ forms 80-90 % of the dust.

The volatilisation depends on furnace temperature. Figure 3 shows measured particulate emission levels as a function of the maximum crown temperature in an industrial gas fired soda-lime glass furnace. Practical observations and measurements show the increased levels of particulate emissions at reducing combustion conditions in the furnace atmosphere, enhancing pure lead and sodium volatilisation.

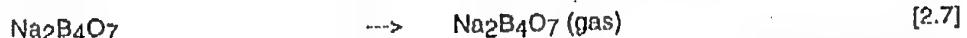
Borosilicate glass furnaces

In borosilicate glass furnaces, the particulates contain the relatively volatile components: sodium, potassium and boron oxides. Similar to soda-lime glass furnaces, the volatilisation from the molten glass or from the batch blanket probably can be regarded as the major source for emissions of sodium borate, potassium borate, potassium sulfate (in oil fired furnaces or during melting of sulfate containing glasses) and boric acid particulates.

Boron volatilisation from the batch blanket can be reduced by using alkali or earth alkali borates instead of boron oxides or boric acid. For insulation wool, borax will be the main boron supplier, for E-glass colemanite (a calcium borate) can be used.

Carry-over of borates can be important for very fine raw materials. However, measurements and the analysis of the particulates (which are mainly sub-micron sized) and the relatively volatile boron species in the flue gases indicate that entrainment of fine particulates will be less important than the volatilisation of boron components.

The next reactions are involved in the vaporisation from batch blankets, containing borax:



The formation of sodium hydroxide is of minor importance according to Fernandes and Cable [17,18], reactions similar to reaction equation 2.8 govern the volatilisation from borax.

At 1000 °C, the vapor pressures of NaBO₂ and Na₂B₄O₇ have been calculated from thermodynamic data given in reference [16], the equilibrium pressures of these sodium borates are in the range of 20-40 Pascal (0.0002 till 0.0004 bar or 200-400 volume-ppm). The vapor pressures of boric acids and sodium hydroxide in equilibrium with borax and in a wet furnace atmosphere with 15 vol.-% water are much lower at 1000 °C: about 5-10 Pascal.

At temperatures above 1000 °C reactions between the sand grains, borax and other raw material components take place and the chemical activity of the borax drops but the much higher temperatures still increase the volatility of boron species.

The calculated equilibrium vapor pressures above sodium borosilicate melts at 1500 °C are in the range of about 500-3000 Pascal for NaBO₂ and 200 till 500 Pascal for HBO₂ (in an atmosphere with 15 vol.-% water vapor). This means that volatilisation of boron and sodium species from borax during the melting of the batch blanket will be neglectable, compared to the volatilisation process from the molten glass at higher temperature levels.

For calcium borate raw materials the batch blanket volatilisation reaction can be described by:



Frischat and Herr [19] measured up to 1200 °C the volatilisation from colemanite (2 CaO, 3 B₂O₃, 5H₂O) in wet atmospheres. At 1000 °C, colemanite appeared to give less volatile losses than ulexite (Na₂O, 2CaO, 5B₂O₃, 16H₂O) or tin calconite (a borax component: Na₂O, 2B₂O₃, 5H₂O). Volatilisation losses from borax at 15 vol.-% water containing atmospheres and 1000 °C are about twice the losses from colemanite under the same conditions.

In dry atmospheres, for temperatures not exceeding 1100 °C, volatilisation losses from borax, colemanite or ulexite are very low.

Frischat assumed the volatilisation of mainly sodium metaborates or boric acid. The appearance of volatile calcium borate compounds is neglectable.

From practical observations, measured volatilisation rates and literature data [17-26], the next conclusions can be drawn:

- a. A depletion of boron at the surface layers will occur in stagnant borosilicate melts after a few hours. The depletion rate increases with the water vapor pressure and viscosity. The depletion at high humidities may lead to a very low volatilisation rate of the borates from the melt after several hours [8]. Depletion is of minor importance in: dry atmospheres, at higher convection currents at the surface or within short time periods.
- b. KBO₂ and NaBO₂ are the most important volatile components during alkali-boro-silicate melting. Alkali borates and boric acid are the major volatiles from E-glass melts. According to Oldfield and Wright [20], Na₂B₄O₇ may be an important volatilisation product if the molar ratio of B₂O₃: Na₂O in the melt exceeds the value of 2.
- c. At temperatures above 1200 °C, sodium metaborate or potassium metaborate and metaboric acid (HBO₂) are the most important boron containing components in the flue gases. H₃BO₃ becomes important below 1000 °C by reaction of HBO₂ and H₂O. During cooling all kind of borates can be formed like: K₂O, 2B₂O₃, K₂O, 3B₂O₃, K₂O, 4B₂O₃, K₂O, 5B₂O₃ or sodium borates. These borates form particulates below 800 °C. Condensation might take place at very low flue gas temperatures (for instance H₃BO₃ condensation below 150 °C) or hydration of the borate dust might occur (this will increase the total weight of the dust).
- d. Potassium oxides and sodium oxides in the melt in combination with boron oxide will have comparable and relatively high volatilisation levels.
- e. The activity coefficient of B₂O₃ in the molten borosilicate glasses is much higher than the alkali oxide activity coefficients. This leads to very high volatilisation rates of boron species from borosilicate melts compared to soda-lime-silica melts.
- f. In borosilicate melts containing > 5 wt-% alkali oxides, alkali metaborate volatilisation appears to be much more important than metaboric acid (HBO₂) and alkali hydroxide formation. The particulates in the flue gases will exist mainly of sodium borates. The water concentration in the furnace atmosphere is of minor importance for the sodium and boron volatilisation in these cases (> 5 % alkali-oxides in the borosilicate melt), according to Conradt [8] and Wenzel [12]. This probably will be the situation for C-glass melting (insulation fiberglass), the higher water concentrations in the furnace atmosphere during for instance oxy-fuel firing hardly contributes to the boron losses for this glass.

Oxy-fuel combustion with much lower gas velocities above the melt compared to conventional fired furnaces, will probably lead to much lower specific particulate emissions levels (given in emissions per ton of molten glass) in insulation glass wool furnaces.

- g. Metaboric acid is the major component, volatilizing from E-glass melts with very low alkali oxide concentrations (< 1 mol-%). Volatilization of this component is dependent on the water vapor pressure in the furnace atmosphere.
- h. The most important emissions from E-glass furnaces are: potassium borates, boric acid, some potassium/sodium sulfates (in oil fired furnaces or using sulfates as flining agents) and HF.
For insulation wool, borosilicate glass furnaces, the particulates contain mainly sodium borates.

Lead glass furnaces

In lead glass furnaces also volatilisation from the molten glass appears to be the major cause of the particulate emissions. Typical dust compositions for these furnaces are: 60-70 % PbO, 10-20 % K₂O, some arsenic compounds, some Na₂O (probably as NaCl or Na₂CO₃). The lead volatilises [21] from the melt as lead oxide (PbO) or Pb(OH)₂. Some NaOH and especially KOH will also vaporize from the alkali containing lead glass melts. At local reducing conditions pure Pb-vapors might be released from the melt.

Modelling of volatilisation and particulate formation

Models have been proposed [8,13] and used [28] to predict the effect of glass composition, gas velocity above the melt, glass melt surface temperature and furnace atmosphere composition on volatilisation rates and expected particulate emission levels. Other models have also been developed to calculate condensation rates and deposition rates in flue gas systems, regenerators and recuperators [16].

Figure 4 shows as an example results of modelling studies for soda-lime glass melts.

4 Conclusions and recommendations

Knowledge about the sources of emissions in glass furnaces is requested in order to find the most efficient primary measures for reducing the release of particulates, SO_x, HCl, HF, selenium components, heavy metals and NO_x into the environment.

Today, the origin of particulate emissions from soda-lime glass, borosilicate and lead glass furnaces are well understood.

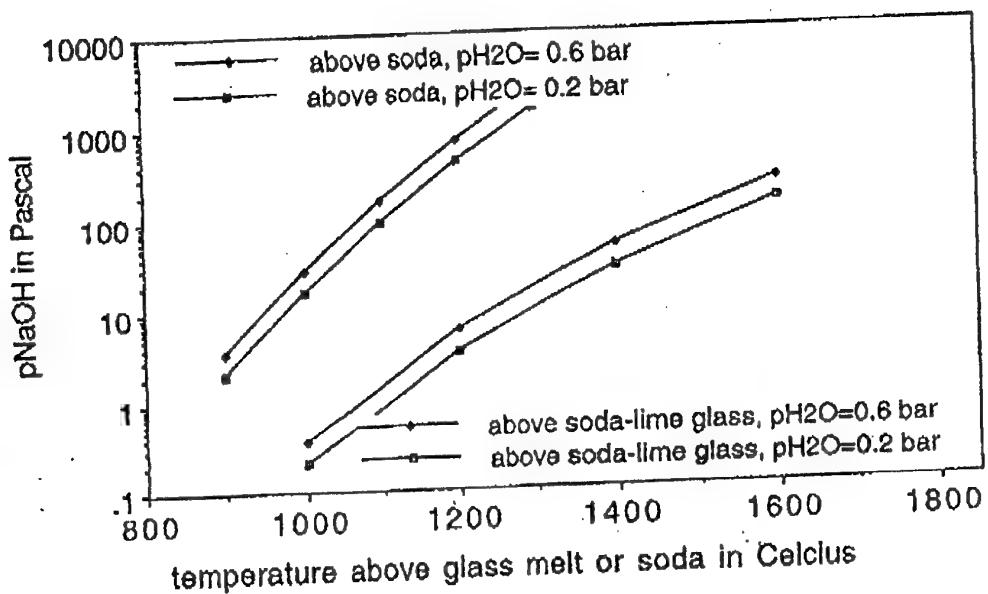
Volatilisation from the batch blanket and melt is the most important process leading to particulate, boron, HCl, HF and selenium emissions. The choice of the raw materials determines the HCl and HF emissions. Different process conditions, the combustion process and temperature of the glass melt surface or gas velocities above the melt have an impact on volatilisation rate and particulate emission levels.

Volatilisation models have been applied to obtain a quantitative understanding on the effect of glass melt surface temperature, glass composition, stirring, gas velocity above the melt and furnace atmosphere on emission levels.

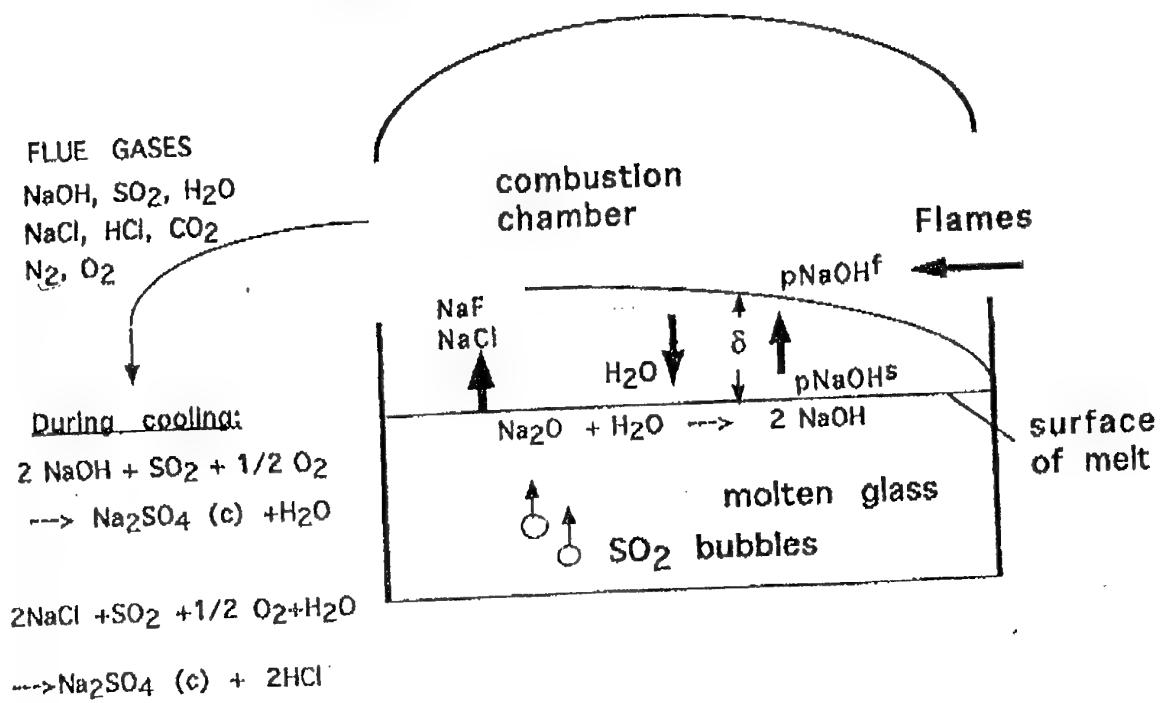
Properties of Molten Glass

Volatilisation

7



1 NaOH equilibrium vapor pressures above soda and soda-lime-silica melts (12 wt.-% Na₂O) in water vapor containing atmosphere

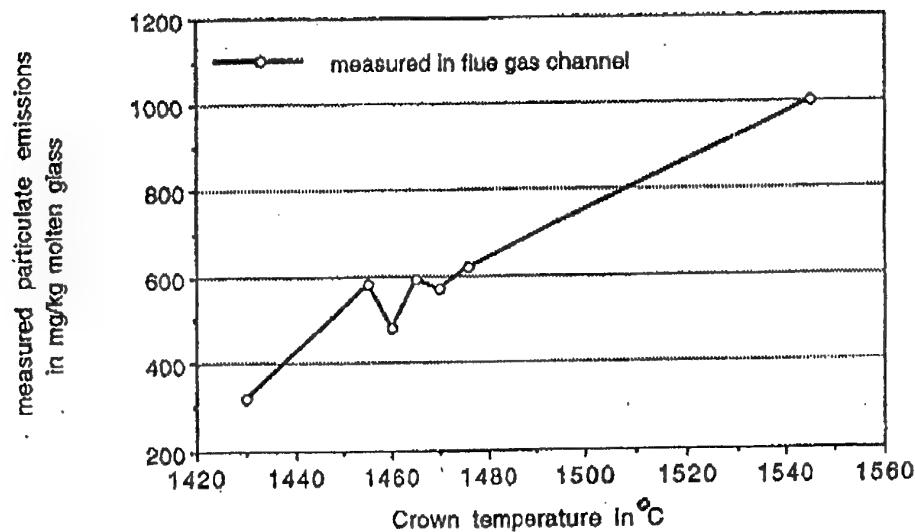


2 Volatilisation mechanism for sodium from soda lime glass melts and condensation reactions during cooling

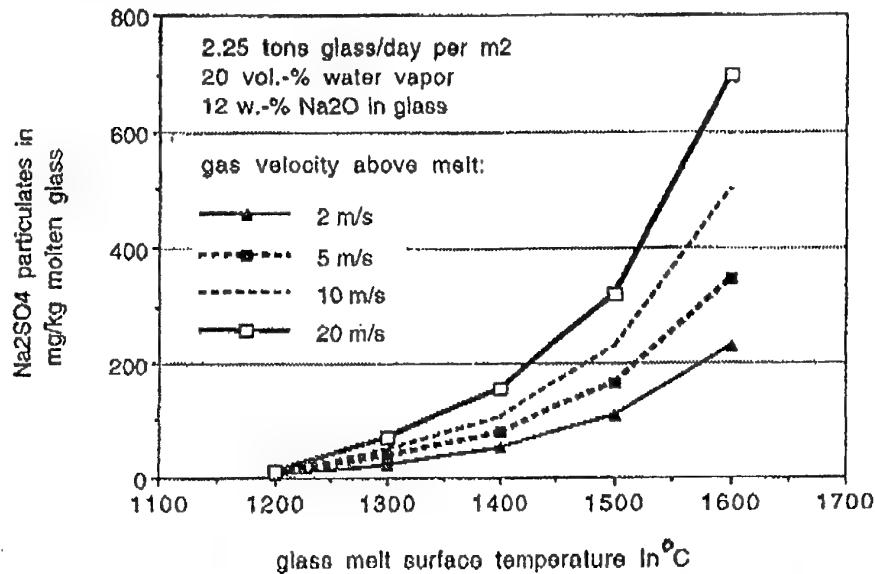
Properties of Molten Glass

Volatilisation

8



3 Effect of increase in crown temperature (reflecting increase in glass melt temperature) on particulate emissions of a recuperative soda-lime silica glass furnace (existing industrial case)



4. Results of a modelling study on the effect of gas velocity and glass melt temperature on particulate emissions due to NaOH volatilisation from soda-lime glass melts [28]

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Glass Surfaces 1

INTRODUCTION TO GLASS SURFACES

This lecture will describe the important physical and chemical characteristics of multicomponent silicate glass surfaces. Subsequently, the way these characteristics influence the optical, mechanical, chemical and electrical properties of glass will be summarized. An emphasis will be placed upon the important role the surface plays in controlling the mechanical strength of glass. The concepts of fracture mechanics, flaw sensitivity, and crack-growth will be introduced.

Glass Surfaces 2

CHARACTERIZATION OF GLASS SURFACES

The emphasis in this lecture will be placed on methods for surface compositional analysis and in-depth profiling of glass; for example, x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Fourier transform infrared spectroscopy (FTIR), and electron microprobe analysis (EMPA). Selected methods for characterizing the physical morphology of glass surfaces--for example, electron microscopy (SEM) and atomic force microscopy (AFM)--will be included. Finally, the most common methods for studying the strength behavior of glass will be reviewed.

Glass Surfaces 3

SURFACE CHEMISTRY OF GLASS

The surface chemistry of silicate glasses is dominated by the behavior of water. The fundamental aspects of this interaction will be described for silica glass, and then these concepts will be extended to include the behavior of more complex multicomponent glasses. This will lead naturally into a discussion of leaching, weathering and corrosion. These phenomena are of practical relevance to commercial glass manufacture and applications. Finally, the unique behavior of hydrofluoric acid, and the role of surface chemistry in glass polishing, will be described.

Glass Surfaces 4

MANUFACTURING EFFECTS ON GLASS SURFACES

The primary goal of this lecture will be to familiarize the participants with the important physical and chemical characteristics of float glass, container glass and fiberglass surfaces. This lecture will also serve to summarize this series of lectures by exemplifying the use of various characterization methods to understand the relationship between surface chemistry, manufacturing processes and the performance of the fabricated glass object.

GLASS SURFACES

by

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- In practice, the glass surface is defined by the region that *INFLUENCES* the property or function of interest.

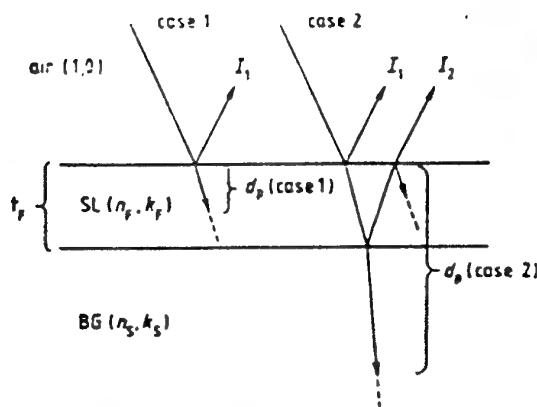
Adhesion---> molecular dimensions(0.1-1.0 nm)

Strength---> 1.0nm -100um

Chemical Durability---> 10-100nm

Optical---> 10nm-10um

leached
layer →
BULK



FTIR Reflectance

Figure 1. Reflections of incident beam for an optically thick (case 1) and optically thin (case 2) modified surface layer (SL with thickness t_f and constants n_f, k_f) on unmodified bulk glass (BG with n_s, k_s). d_p = penetration depth for the two cases. For thick film: measured reflectance $R = I_1$; for thin film: $R = I_1 + I_2 +$ other terms.

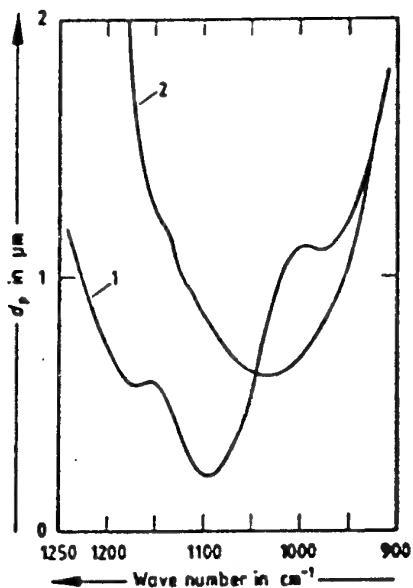
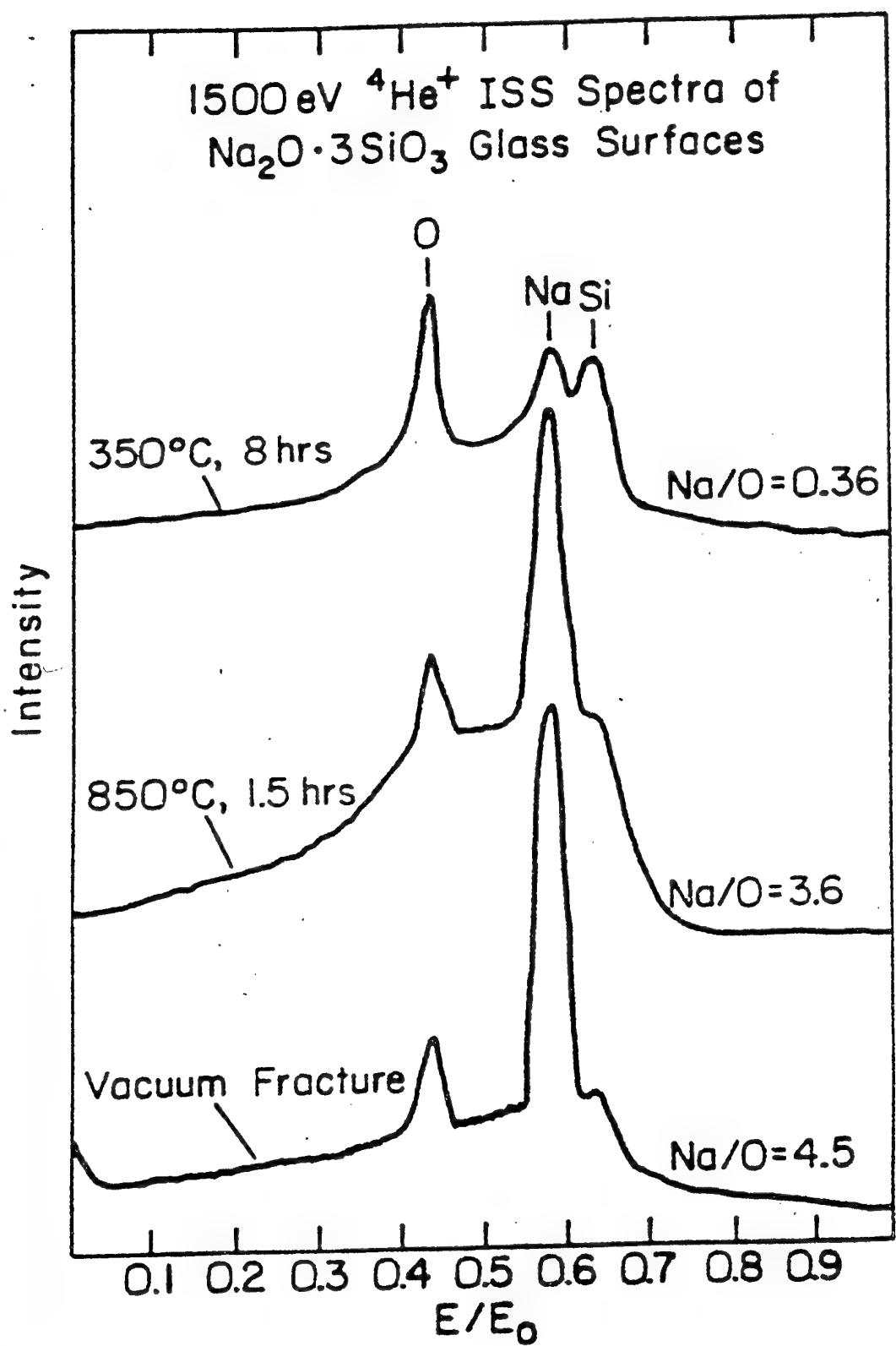


Figure 2. Spectral behavior of the penetration depth, d_p , computed between 1250 und 900 cm^{-1} according to equation (3) for bulk SiO_2 glass [18] (curve 1) and soda-lime glass [20] (curve 2).



ISS

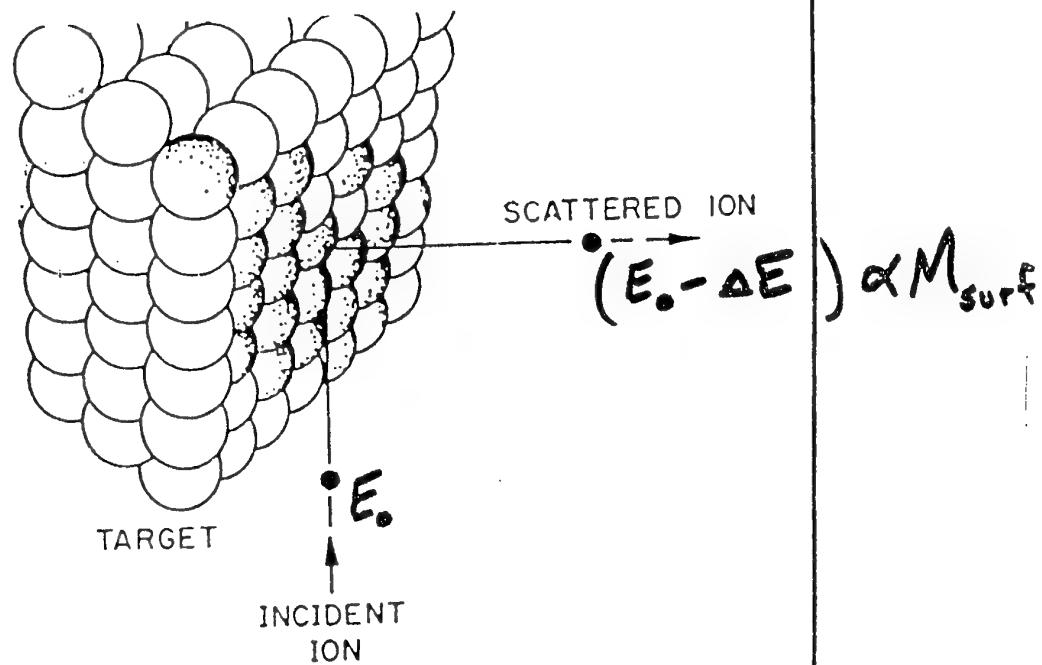
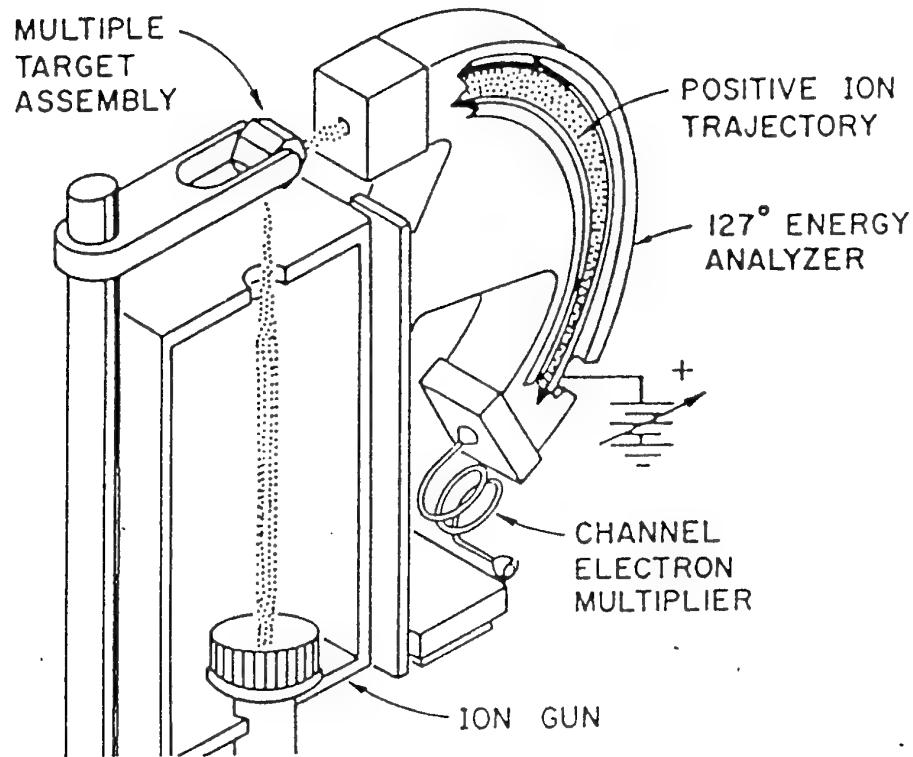
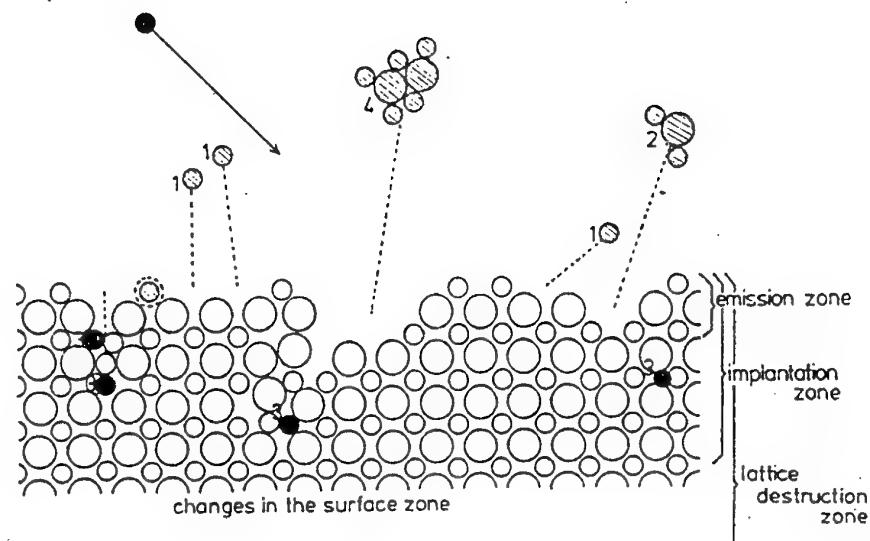
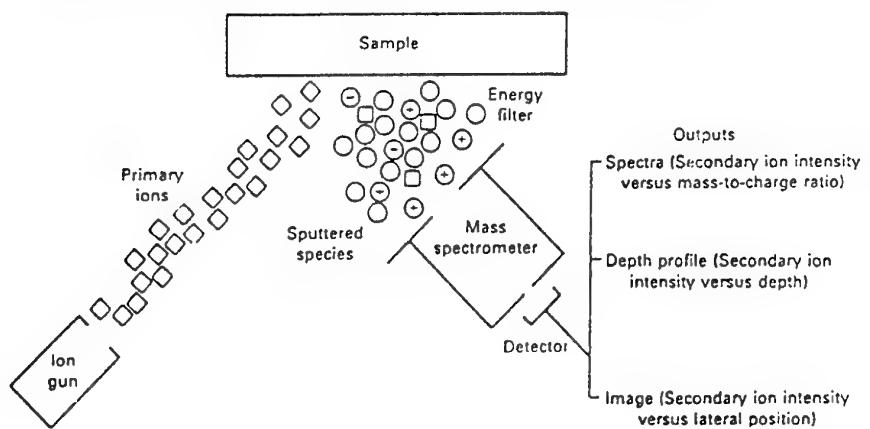
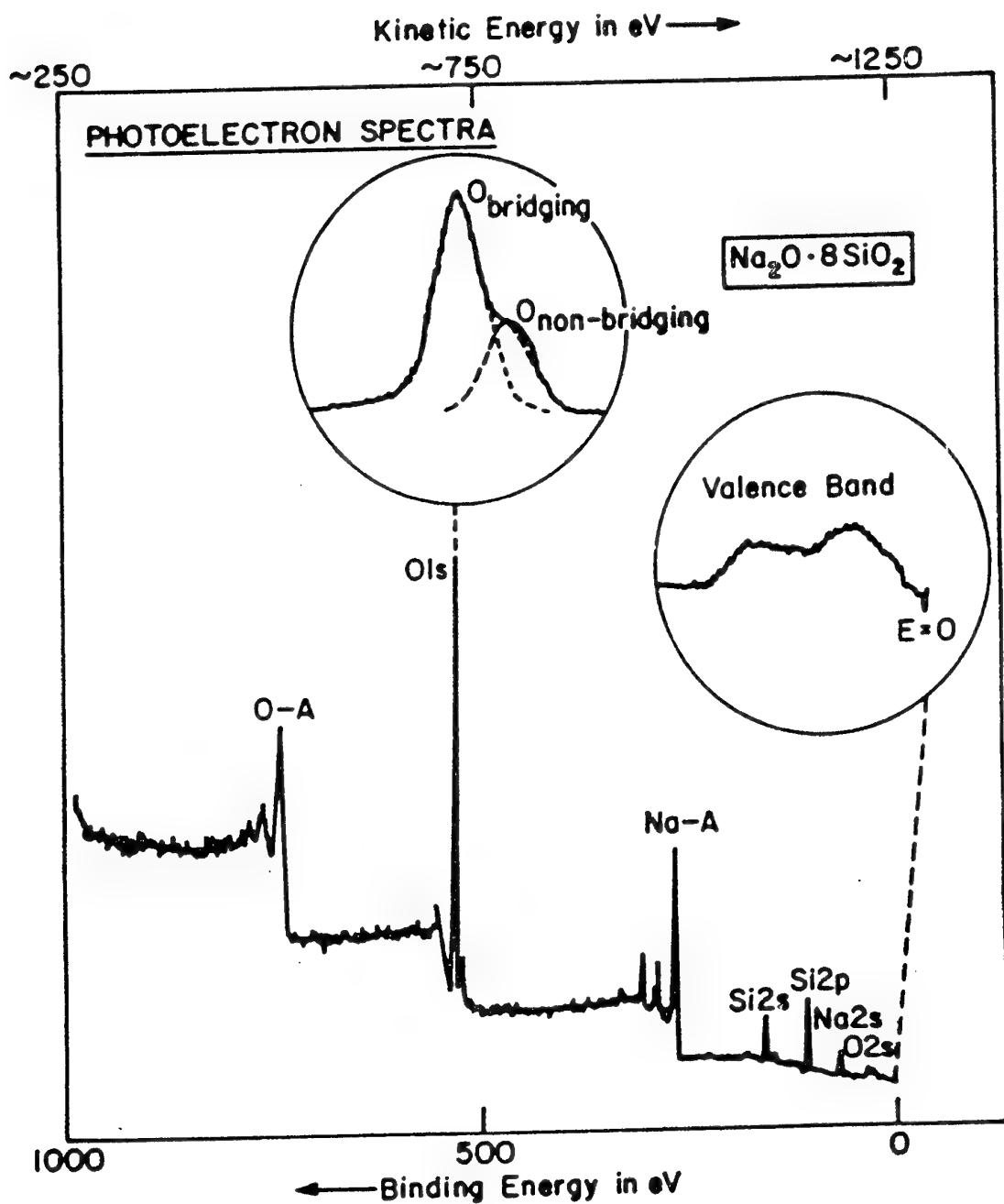


Fig. 1 Schematic representation of the principles of SIMS





XPS X-Ray Photoelectron Spectroscopy

AES Auger Electron Spectroscopy

ISS Ion-Scattering Spectroscopy

SIMS Secondary Ion Mass Spectroscopy

SIPS Sputter Induced Photon Spectroscopy

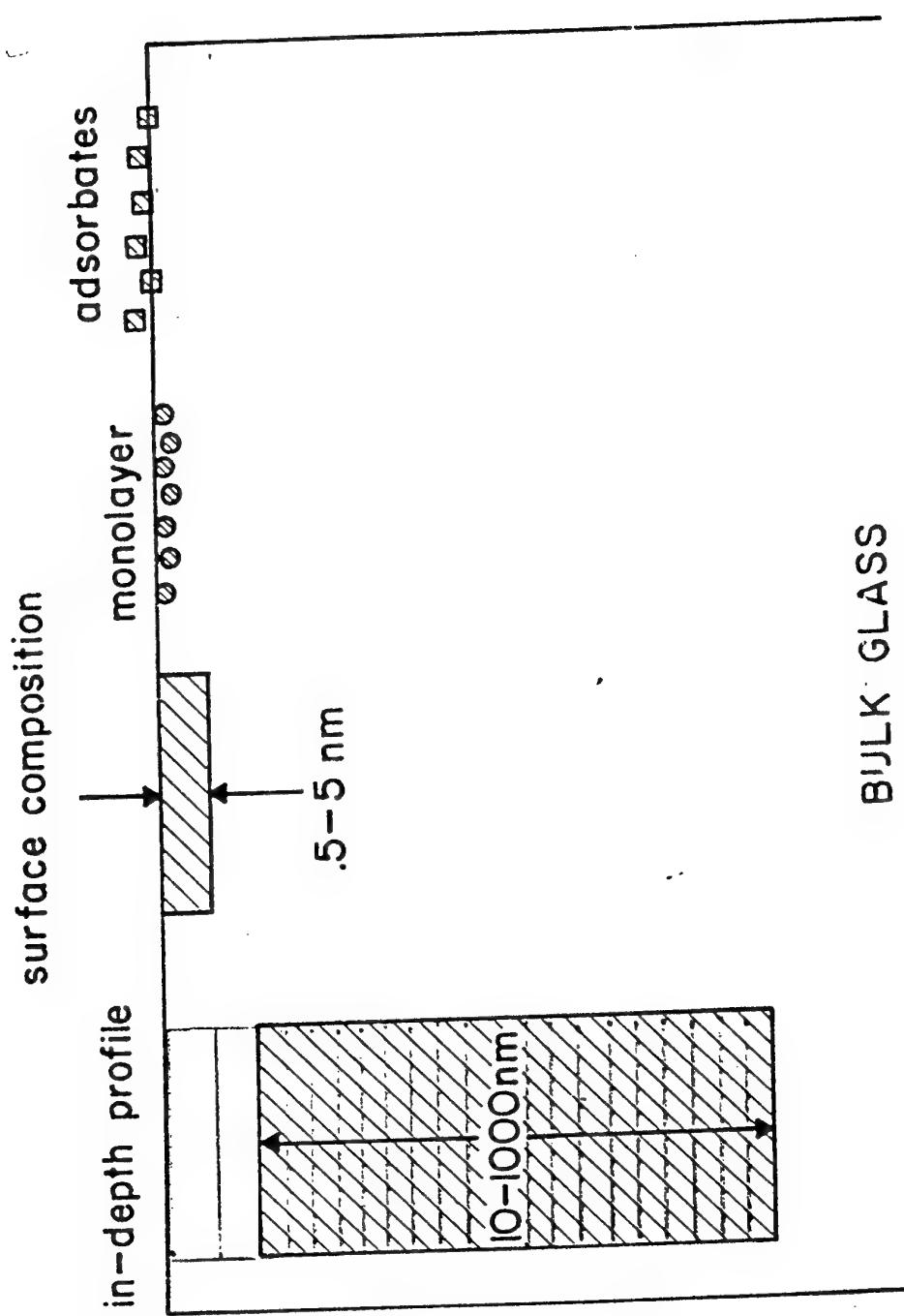
SNMS Secondary Neutral Mass Spectroscopy

RBS Rutherford Backscattering Spectroscopy

ERD Elastic Recoil Detection

NRA Nuclear Reaction Analysis

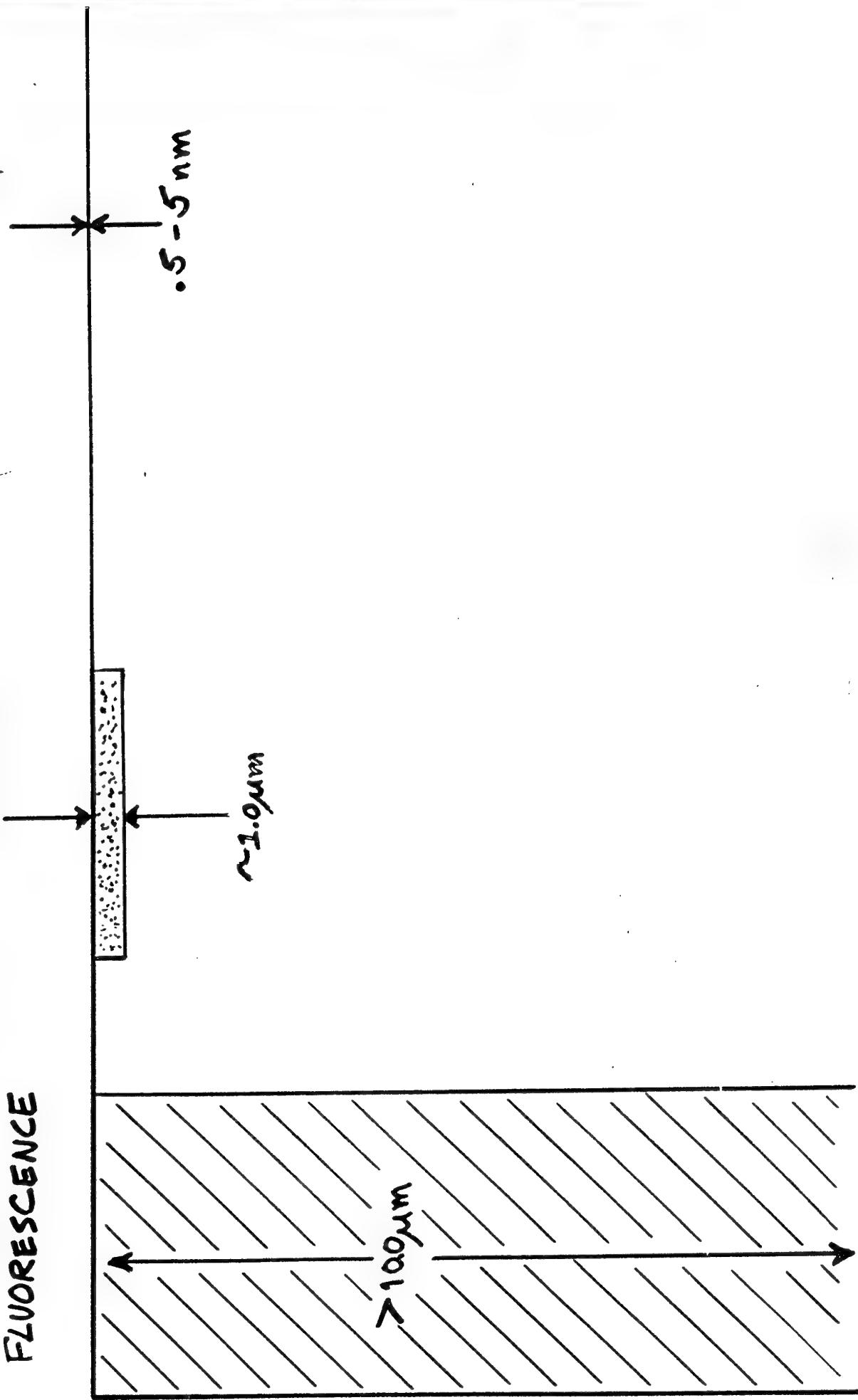
SSIMS Static-SIMS



SURFACE ANALYSIS TECHNIQUES

ELECTRON MICROPROBE

X-RAY FLUORESCENCE



CHARACTERIZATION OF GLASS SURFACES

1. General objectives of glass surface characterization
2. Methods for surface compositional analysis and depth-profiling
 - XPS - *surface composition*
 - SIMS - *in-depth profiles*
 - static SIMS - *organics and water*
 - ISS - *in the surface MONOLAYER*
 - ERD - *hydrogen*
3. Other methods for glass surface analysis
 - FTIR/IRRS
 - AFM

MANUFACTURING EFFECTS ON GLASS SURFACES

1. Float Glass

- tin penetration
- tin bloom
- corrosion and weathering
- (strength)

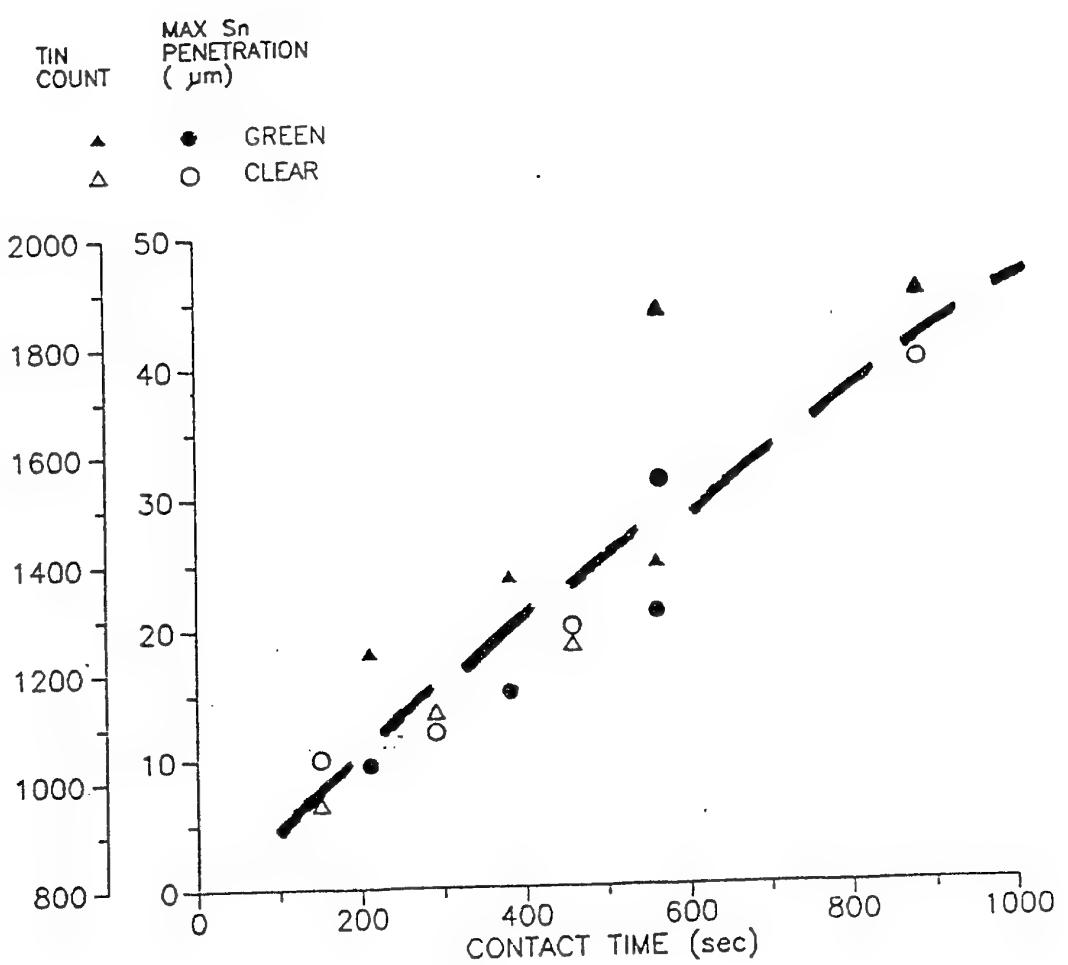
2. Fiber Glass

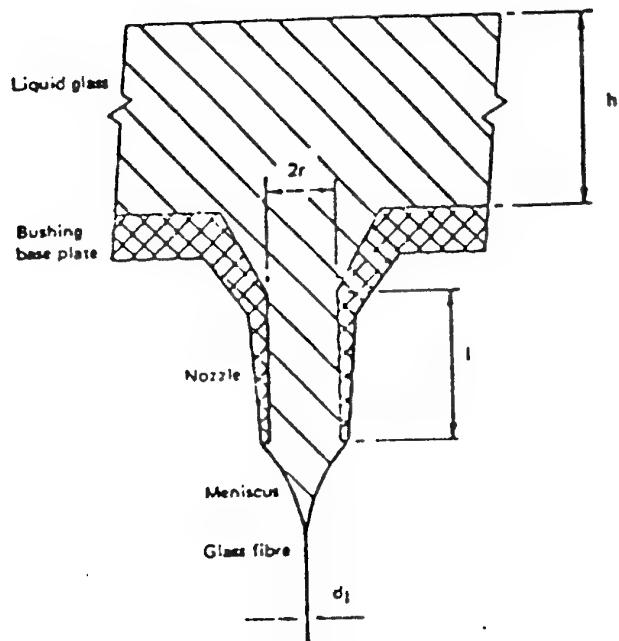
- water adsorptivity
- solubility
- silane adsorption

3. Container Glass

- strength
- external coatings
- internal surface treatments

4. (Sol/Gel Surface Chemistry)

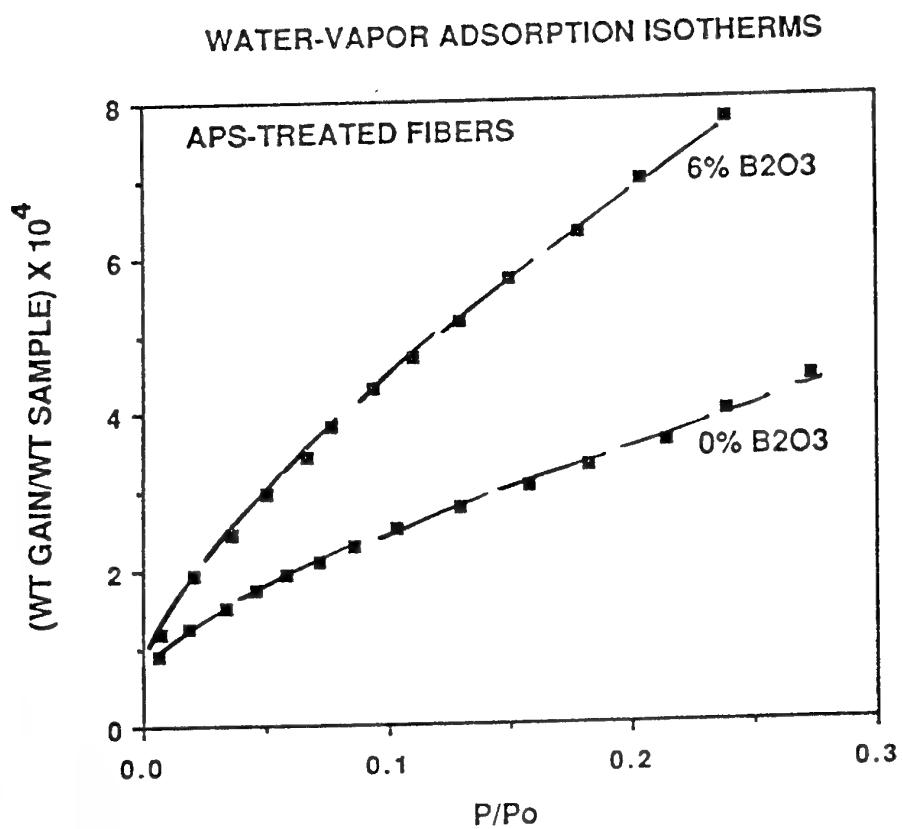




The nozzle in a base plate of a bushing showing the meniscus formed during attenuation of the glass into fibre

- the strength and surface reactivity of glass fibers is established at the molecular and intermediate - range level
 - chemical ordering; CaO , CaAl_2O_4 , CaB_2O_4 , $[(\text{Al},\text{Si})\text{O}_4]$
 - microheterogeneity
 - dissolved gases
 - bulk and surface water
 - surface structure; relaxation and hydration
- - and influenced by
 - melting history
 - forming rate
 - forming atmosphere
 - coatings

- 6% B_2O_3 fibers adsorb significantly more water-vapor than 0% B_2O_3 fibers.



SUMMARY

- Boron-oxide enhances the adsorption of aminosilane
- The silane adsorption is multilayer at long aging times
- The silane treated fibers adsorb more water vapor than the untreated fiber
- This water adsorption capacity is enhanced by B_2O_3
- Soluble constituents of the glass influence the condensation of silane

→ Condensation of Silane w/ Al, F & Na
→ Water Adsorption on
Sized Fibers

Strength Reduction due to Handling Quality

The following strength data were collected after simulated handling damaged occurring at 300°C. The inside of the bottles were abraded in case the outside had already been damaged.

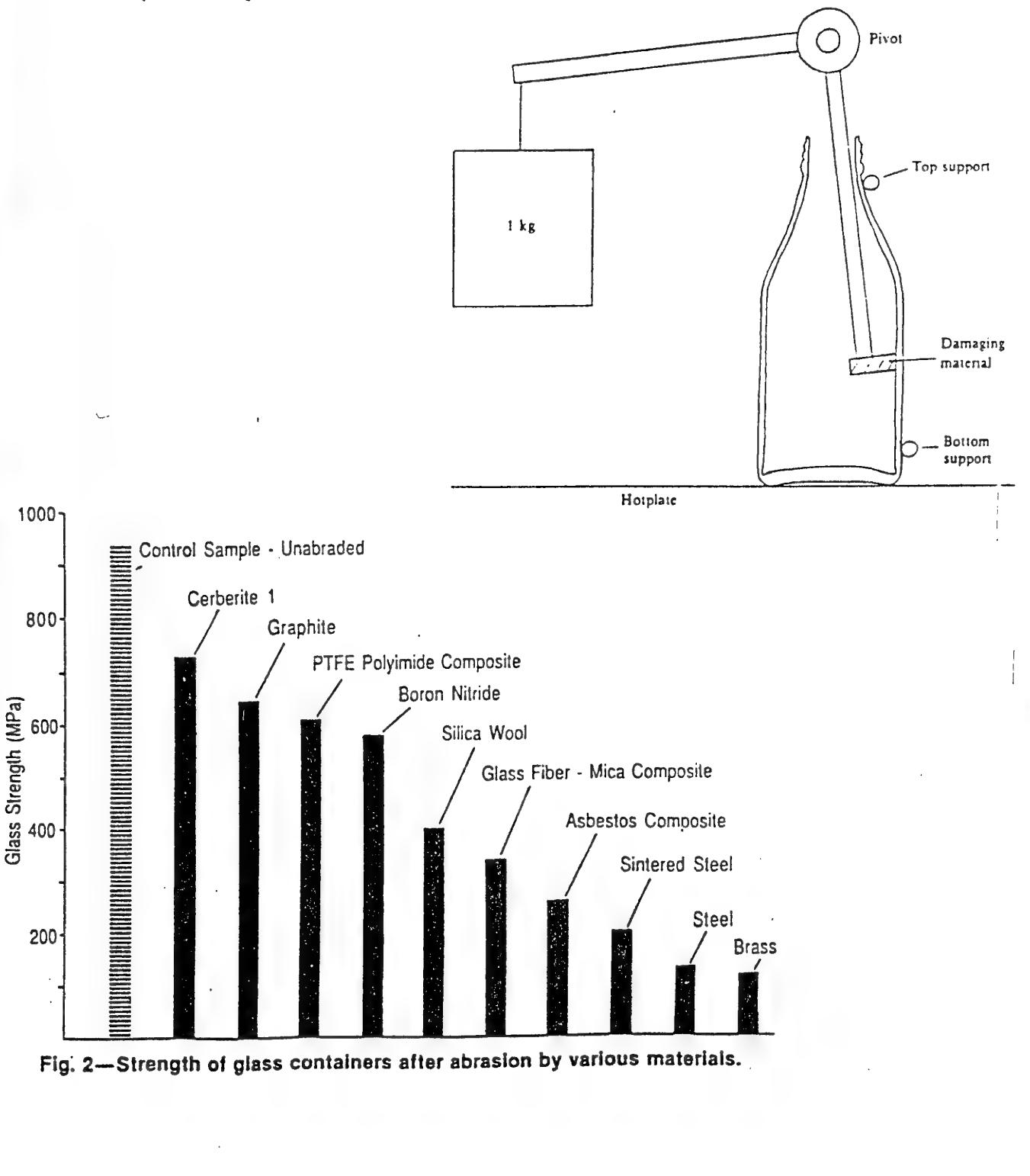


Fig. 2—Strength of glass containers after abrasion by various materials.

Coatings on Glass Containers

- In almost every instance, two coatings are currently applied to bottles. The first is the "hot-end" coating (typically SnO_2) for strengthening, and the second is the "cold-end" coating (poly(ethylene) emulsions, oleic acid) to protect and lubricate the bottles.

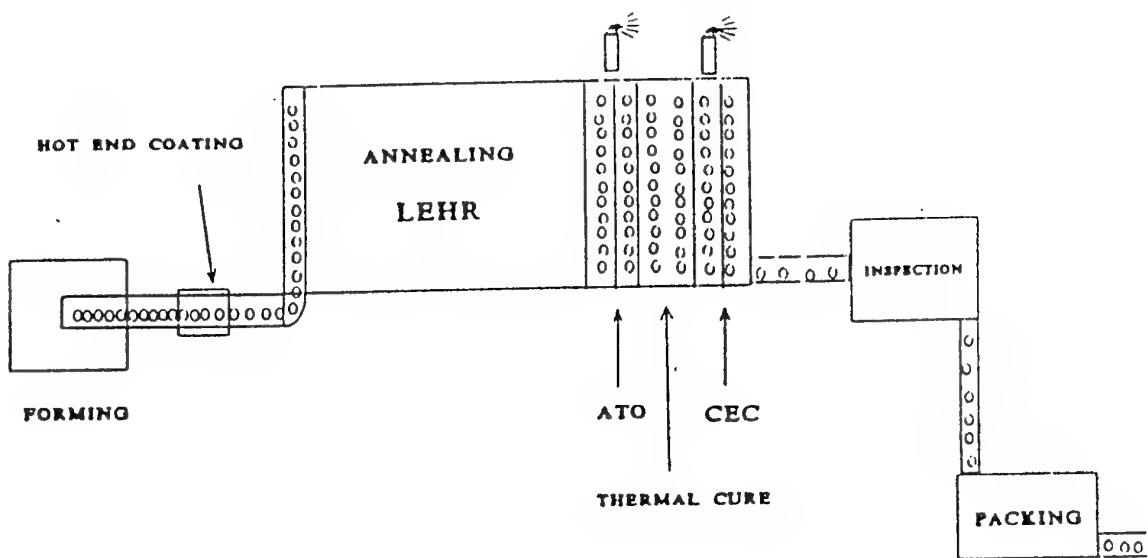


Fig. 3. Glass container strengthening line.

CONCLUSIONS

- dehydrated surfaces show only isolated Si-OH and B-OH
- Si-OH is more effectively *isolated* on E-gel than silica gel
- water adsorption is faster and more tenacious on the E-gel
- the unsaturated Lewis acid sites (Al^{III} and B^{III}) and oxygen's associated with Ca⁺⁺, may account for this
- silane adsorption, and hydrolysis, occurs preferentially at B-OH

- The surface composition and chemistry of glass is not a constant nor does it equal the bulk
- The effects of high temperature manufacturing processes may be characterized and controlled within limits
- Nevertheless, surface chemistry can vary continuously during subsequent exposure to humid atmosphere
- Cleaning seldom reproduces a standard surface condition
- Chemical processing of glass surfaces can, in principle, create reproducible conditions

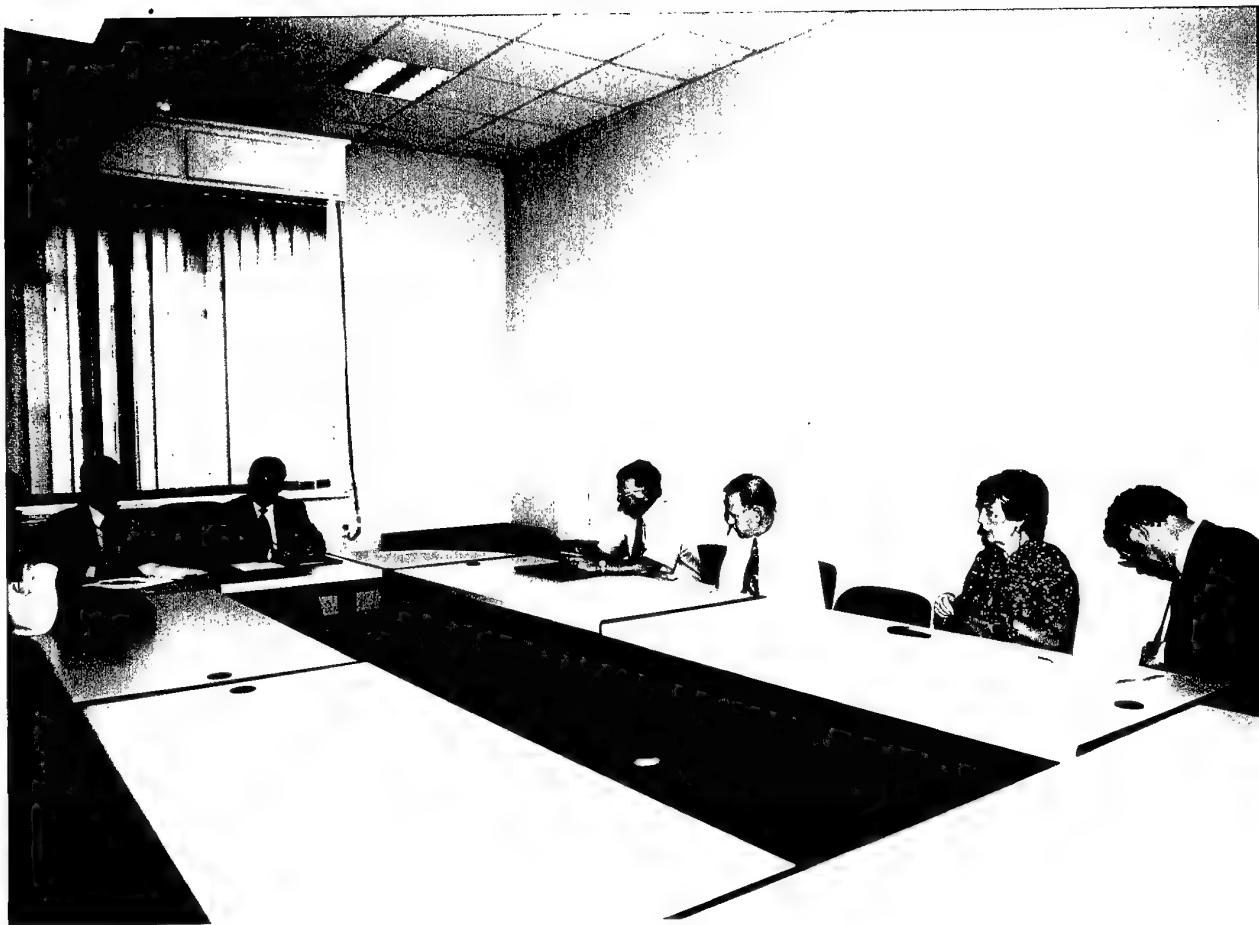
- There are still “characteristics” of glass surfaces that influence weathering, corrosion, adhesion and strength that are “invisible” to the currently available methods of analysis.

Photographic Registration For The Workshop Events

This Part is Restrictedly Distributed In NRC and USAF-EOARD



A general view for the NRC , Dokki, Cairo,Egypt
An announcement for the workshop is hanged on the main gate.



**Meeting of Prof. Dr. Nabil Saleh ,
president of NRC,
with the distinguish lecturers on 23.9.1996.**

Announcement for Journalist

**The First Workshop in The Technology Transfer Program on:
Frontiers of Advanced Materials and Technology**

under the supervissoin of

**Prof. Dr. Nabil. A. Saleh,
HONORARY CHAIRMAN.
President of**

**the National Research Centre,
Cairo - Egypt**

in cooperation with:

**United State Air Force - European Office of Aerospace Research and
Development, London - UK**

at
The conference Hall - The National Research Centre
, Dokki, Cairo, EGYPT
on
23 - 26, September, 1996

The workshop is Organized by:

Osama H. El-Bayomi, U.S. Air Force - EOARD, London, UK.
Morsi M. Morsi, Prof. of Glass Science and Technology, NRC, Egypt.

Topics :

Bioactive Medical and Dental Materials : 1) Clinical needs and types of biomedical materials.
2) Tissues and their reaction to implants. 3) Principles of bioactive bonding. 4)
Medical and dental application of bioactive implants.

Sol Gel Optics Technology: 1) Principles of sol-gel processing . 2) Gel silica optics, micro-optics and surface diffractive optics. 3) Porous gel silica matrices for hybrid optics. 4) Concepts of commercial principles of technology transfer and entrepreneurship.

Infra-red Transmitting glasses: 1) glass forming systems. 2) Optical properties of IR glasses
3) IR glass optical fibers. 4) Rare- earth doped glasses(optical amplifier, fiber laser). 5) IR glasses for integrated optics.

Fundamentals of Industrial glass melting: 1) Introduction into Modern Glass Manufacturing.
2) Batch Melting, 3) The fining process. 4) Volatilization and dust formation in glass furnaces. 5) Foam formation during glass melting.

Glass Surfaces: 1) Introduction. 2) Characterization of glass surfaces. 3) Surface Chemistry.
4) Manufacturing effects on glass surfaces.

**The First Workshop in The Technology Transfer Program on:
Frontiers of Advanced Materials and Technology
23 - 26, September, 1996**

Summary

This workshop will discuss five topics given by distinguish guests from England, France, and USA. The topics are useful in the fields of dental implants, surgery, glass industry, optics and chemical industry.

The sol-gel method will be presented and its utilization in preparation of optics will be given as an example.

Attention will be given to biomaterials, which are the most important synthetic materials for reconstruction of the body.

As examples for the utilization's of the bioactive materials, certain compositions of glasses, ceramics, glass ceramics and composites have been shown to bond to bone, fill the gaps between bone and living tissue or to coat inert implants, or to replace missing bone which become infected or cancerous or even for radiation treatment where they are injected and the blood stream carries them to kill the cancer cells without serious side-effects.

The present workshop will discuss also the IR. transmitting glasses which have potential applications in night -vision systems, telecommunication links and temperature sensors.

Modern technology in industrial glass melting, and the relation between the material properties and the melting process will be presented.

The role played by the glass surfaces in determining of its chemical & physical properties will be discussed.

In short , the present workshop will through light on advanced glassy materials and the technology of its preparation as a first step to enhance its introduction to the Egyptian market. On the other hand, the workshop will, also , discuss the technology of improving product quality and product performance to fulfill the international standards.

The objectives of the NRC Technology Transfer Program are to:

- 1-Through light on the technologies and materials that could be new subjects for manufactures who wishes to generate productive new business.**
- 2- Through light on new areas for research and development.**
- 3- Through light on latest developments in manufacturing industries.**
- 4- Acknowledge with experts and distinguish scientists in the intended areas.**

Opening Session

**Prof.Dr.Morsi M. Morsi
(Organizer frof NRC)
Presenting his speech in the opening session**





Speech of :
Prof. Dr. Morsi M. Morsi
(coordinator form NRC)

on the occasion of opening the first workshop in
Technology transfer program on frontiers,
23 Sept. 1996

Mr. President,
distinguish guests
Ladies and gentlemen

Welcome you all in the first workshop in the technology transfer program on .

This workshop will discuss five topics given by distinguish guests from England, France, and USA. The topics are useful in the fields of dental implants, surgery, glass industry, optics and chemical industry.

The sol-gel method will be presented and its utilization in preparation of optics will be given as an example.

Attention will be given to biomaterials, which are the most important synthetic materials for reconstruction of the body. The materials are generally no different in structure and properties to materials used in chemical, aerospace or nuclear industries. It is the matching of the properties of materials and unique requirement of surgical reconstruction, that is the key to biomaterial science.

Biomaterials may include in general, metals, polymers, glass, ceramics and composites.

As examples for the utilization's of the bioactive materials, certain compositions of glasses, ceramics, glass ceramics and composites have been shown to bond to bone. Some more specialized compositions of bioactive glasses will bond to soft tissues as well as bone.

Some bioactive glass granules can fill the gaps between bone and living tissue or to coat inert implants, or to replace missing bone which become infected or concerous .

Glass microspheres containing certain radio active isotope are used for radiation treatment where they are injected through a catheter placed in an artery and the blood stream carries them to kill the cancer cells without serious side-effects.

The present workshop will discuss also the IR. transmitting glasses. These materials have potential applications in night -vision systems, telecommunication links and in laser and amplification purposes. They are used also in pyrometry and remote IR spectroscopy.

The industrial glass melting, methods of firing and reducing energy consumption, glass melting problems, and the relation between the material properties and the melting process will be discussed.

The role played by the glass surfaces in determining of its chemical & physical properties, and methods of surface compositional analysis will be discussed. Emphasis will be given to the relation between surface chemistry, manufacturing processes and the performance of the fabricated glass object.

In short ,it can be said that the present workshop will through light on advanced glassy materials and the technology of its preparation as a first step to enhance its introduction in the Egyptian market. On the other hand, the workshop will, also , discuss the technology of improving product quality and product performance to fulfill the international standards.

It is hoped that the NRC Program of Technology Transfer will also through light on :

- 1-Technologies and materials that could be new subjects for manufactures who wishes to generate productive new business.
- 2- New areas for research and development.
- 3- Latest developments in manufacturing industries.
- 4- Experts and distinguish scientists in the intended areas.

At the end of my speech I would like to express my appreciation : to Prof. Dr. Nabel Saleh president of the NRC for his continuos support and supervision of this workshop.

My deep appreciation to Dr. Osama El Bayomi (coordinator - from EOARD) for his support and continuos cooperation during coordinating of this workshop.

Thanks are also due to the United Air force European Office of Aerospace Research and Development for its contribution to the success of this workshop.

My thanks and appreciation to the distinguish guests ,Dr. J. wilson Hench, Prof. Dr. L. Hench, Prof. Dr. J. Lucas, Prof. Dr H. De Waal and Prof. Dr. C. Pantano for accepting the invitation to participate in this workshop.

My thanks to members of the advisory committee Prof. Dr. El-Mallawani & Dr. M. Hindawy, and to many of my colleges and administrators members in the NRC for their cooperation and assistance.

Thank you for attending this workshop hoping to see you again in the second workshop in this program

Morsi. M. Morsi
Organizer- from NRC.

**Prof. Dr. Nabil Saleh
(President of the NRC)
during his talk in the opening session**



متحف التسلووجي في مجال المواد الكيماوية

٢٣ - ٩٦ سبتمبر ١٩٩٦





**Distinguish lecturers
during their talks**

Prof. Dr. Larry Hench

Dr. June Willson Hench,

Prof. Dr. Jacques Lucas

Prof. Dr. Hendrikus De Waal

Prof. Dr. Carlo Pantano





Cairo - - - - -

in cooperation with

U.S. Air Force [0100]
London, Jr.

جامعة الأسنان الدكتور رئيس المركز القومي للبحوث
Technology Transfer

Technology Transfer Program of Advanced Materials and Technology

1997-٩٧ - ٥٤





**Part of the activities
during the welcome reception and breaks between the lectures**









The National Research Centre
Cairo

In cooperation with

U.S. Air Force EOARD
London, UK

تحت رعاية الأستاذ الدكتور / رئيس المركز القومى للبحوث

Technology Transfer Program
Frontiers of Advanced Materials and Technology

برنامج نقل التكنولوجيا في مجال المواد والتكنولوجيا المتقدمة

١٩٩٦ - ٢٦ سبتمبر



Closing Session